

July, 1935

RUBBER CHEMISTRY AND TECHNOLOGY

Published under the Auspices of the
RUBBER DIVISION of the AMERICAN CHEMICAL SOCIETY



VOLUME VIII

NUMBER 3

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RUBBER CHEMISTRY AND TECHNOLOGY

Published quarterly under the Auspices of the Rubber Division
of the American Chemical Society,
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Vol. VIII

July, 1935

No. 3

CONTENTS

General Subjects

	PAGE
Rubber Division Activities.....	xxiii
New Books and Other Publications.....	xxvi

Reprinted Papers

The Elasticity of Rubber. By KURT H. MEYER and CESARE FERRI.....	319
Research on Modified Rubbers. VI. The Oxidation of Rubber Solutions with Gaseous Oxygen in Presence of Catalysts. By G. F. BLOOMFIELD and E. H. FARMER.....	335
The Oxidation of Rubber by Hydrogen Peroxide. By B. KAGAN and N. SUKHAREVA.....	352
The Hydrogenation-Cracking of Rubber. By C. M. CAWLEY and J. G. KING.....	360
The Chlorination of Disaggregated Rubber. By B. V. BUIZOV, V. S. MOLO- DENSKIĬ, and N. I. MIKHAILOV.....	371
The Constitution of Rubber and the Nature of Its Viscous Solutions. By H. STAUDINGER.....	375
The Mastication of Rubber. By J. BEHRE.....	388
Plastic and Elastic Phenomena in Rubber. By A. VAN ROSSEM.....	395
Specific Volume, Compressibility, and Volume Thermal Expansivity of Rubber-Sulfur Compounds. By ARNOLD H. SCOTT.....	401

Entered as second-class matter May 12, 1928, at the Post-Office at Easton, Pennsylvania, under the
Act of August 24, 1912.

Refractive Index of Rubber. By ARCHIBALD T. McPHERSON and ARTHUR D. CUMMINGS.....	421
Synthetic Rubber. Its Industrial Production in the U. S. S. R. By I. G. AKOBZHANOV.....	430
Influence of the Gaseous Medium on Hot Vulcanization. By B. V. BUIZOV and M. K. POPOVA.....	437
The Coefficient of Friction of Rubber. By J. B. DERIEUX.....	441
The Specific Gravity of Rubber in Latex. By O. DE VRIES.....	443
The Specific Gravity of Preserved Latex. By EDGAR RHODES.....	448
Heats of Reaction of the System Rubber-Sulfur. By ARCHIBALD T. McPHERSON and NORMAN BEKKEDAHL.....	456
Dispersion of Channel Gas Black in Rubber. By C. R. PARK and V. N. MORRIS.....	470
Surface Chemistry of Carbon Black. By FRANK K. SCHOENFELD.....	483
The Effect of Surface-Active Substances and Electrolytes upon the Crystallization of Sulfur from Rubber Solutions. By B. DOGADKIN and J. MARGOLINA.....	499

RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the editor representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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(2) Any one who is not a member of the American Chemical Society may become an Associate Member of the Rubber Division (and also a member of his local group if desired) upon payment of \$4.00 per year to the Treasurer of the Rubber Division, and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.

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All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, and missing numbers, and all other information or questions should be directed to the Secretary-Treasurer of the Rubber Division, C. W. Christensen, Easton, Pennsylvania, or Rubber Service Laboratories, Inc., Akron, Ohio.

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Rubber Division Activities

The Rubber Division of the American Chemical Society

Officers

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Vice-Chairman.....H. E. SIMMONS, Akron University, Akron, Ohio
Secretary-Treasurer.....C. W. CHRISTENSEN, Rubber Service Laboratories,
Akron, Ohio
Executive Committee.....IRA WILLIAMS, A. A. SOMERVILLE, H. C. CONROY,
J. N. STREET, G. K. HINSHAW
Sergeant-at-Arms.....L. W. BROCK

Minutes of the Rubber Division Meeting in New York City on April 22-23, 1935

The meeting was held in the Ballroom of the Hotel New Yorker with approximately two hundred and eighty in attendance. The following papers were presented.

Thomas Midgley, Jr. American Chemical Industries Tercentenary Contributions of Chemistry to the Rubber Industry.

E. O. Kramer and William D. Lansing. The Molecular Weights of Natural and Synthetic Rubber by the Svedberg Ultracentrifuge.

C. W. Walton and H. J. Osterhof. Reinforcement of Rubber by Pigments. I. Effect of Moisture on Measurements of Heat of Wetting of Gas Blacks.

E. T. Rainier and R. H. Gerke. A Fatigue Cracking Test for Tire Tread Compounds and Some of the Laws of Fatigue.

O. D. Cole. Mixed Reinforcing Pigments in Rubber. I. Effect of Binary Mixtures of Zinc Oxide, Channel Black and Clay upon the Physical Properties.

A. T. McPherson and Norman Bekkedahl. Heats of Reaction of the System: Rubber-Sulfur.

A. E. Warner. Studies on the Variability of Plantation Rubber.

H. L. Fisher and Y. Schubert. The Carbon and Hydrogen Content of Hard Rubber.

George A. Sackett. Consumers' Crude Rubber Requirements.

Dr. Edgar Rhodes, Chief Chemist of the Rubber Research Institute of Malaya, Singapore, F.M.S., followed Mr. Sackett and presented the plantation side of this subject.

The Rubber Dinner was held Monday evening at the Casino de Paree with four hundred and eighty present. The Dinner Committee consisted of A. A. Somerville, *Chairman*, E. B. Curtis, E. W. Schwartz, C. J. Wright, C. R. Haynes, M. N. Nickowitz, R. D. Gartrell, and B. R. Silver, and they are to be congratulated for the dinner and entertainment. The Division wishes also to thank the following companies for their contributions of souvenirs:

L. Albert & Sons St. Lawrence Trading Co. Imperial Color Works
American Zinc Sales Co. Stamford Rubber Supply Midwest Rubber Reclaiming

Ansbacher-Siegle Corp.	Southwark Mfg. Co.	H. Muehlstein & Co.
Binney & Smith	Turner Halsey Co.	National Sherardizing & Machine Co.
Curran & Barry	Wishnick-Tumpeer	Naugatuck Chemical
E. I. du Pont	American Cyanamid Co.	New Jersey Zinc Co.
J. M. Huber	Columbia Alkali Works	Philadelphia Rubber Works
<i>India Rubber World</i>	Flexo Supply Company	<i>Rubber Age</i>
Pequanoc Rubber Co.	General Atlas Carbon	A. Schrader's Sons
Rubber Service Labs.	General Electric Co.	C. J. Tagliabue Mfg. Co.
St. Joseph Lead Co.	Givaudan-Delawanna	R. T. Vanderbilt Co.
United Carbon Co.	U. S. Rubber Reclaiming	

At the close of the papers Tuesday morning a general business session was held. The Secretary made the following report, which was accepted.

Secretary's Report

Total membership to date (April 17, 1935).....		401
Members paid for 1935.....	328	
Associate members paid for 1935.....	73	
New members and associate members for 1935 (in- cluded in above figure).....	34	
Total membership not paid for 1935.....		109
Members not paid for 1935.....	87	
Associate members not paid for 1935.....	22	
New members for 1934 who did not renew for 1935.	20	
Subscriptions paid for 1935.....		107
Subscriptions not renewed for 1935.....	23	
Honorary members and exchanges.....		32

The Treasurer then made the following report which on motion was accepted:

Treasurer's Report

Balance in the bank at Cleveland meeting 1934.....		\$1810.50
Received from dues, subscriptions, and back journals	\$1661.30	
Received from advertising.....	1706.71	
Received from Rubber Manufacturers Assn.....	1500.00	
Received surplus from Cleveland banquet.....	145.60	5013.61
		<hr/>
		\$6824.11
		Forward \$6824.11
Expenses		
Mack Printing Company.....	\$1907.67	
Translations.....	228.89	
Expenses of Secy.-Treasurer to Cleveland, Sept., 1934	20.00	
Postage, office supplies, insurance, long distance, and telegrams.....	36.90	
Secretarial services.....	90.00	
Printing—new stationery, stamps, circular letter, dues slips.....	93.13	

Purchased back numbers for A. H. Gill, Mass. Inst. Tech.....	10.00	
Tax on checks written from Sept. to Feb. 1.....	0.36	
Collection on foreign checks.....	0.44	\$2387.39
		<hr/>
Balance in bank, April 17, 1935.....		\$4436.72
Money in liquidation bank.....		2436.05
		<hr/>
Total.....		\$6872.77

The Chairman named a Nominating Committee consisting of Ira Williams, L. B. Sebrell, and H. L. Fisher, for the election of new officers at the Fall Meeting.

The Rubber Division was fortunate in having present Dr. Edgar Rhodes, of the Rubber Research Institute of Malaya. Dr. Rhodes addressed the Division on "Rubber Production." After a general discussion, the Chairman appointed the following Crude Rubber Committee to contact a Committee to be appointed by the Rubber Research Institute of Malaya with the idea of working toward the elimination of variation in crude rubber: Harold Gray, *Chairman*, G. A. Sackett, W. A. Gibbons, E. B. Babcox, and J. C. Walton.

An invitation was received from A. A. Brill, Chairman of the Akron Rubber Group, to hold the Fall Meeting of the Rubber Division in Akron, Ohio. The Chairman accepted Mr. Brill's kind invitation.

C. W. CHRISTENSEN, *Secretary-Treasurer*

To Members of the Rubber Division Who Contemplate a Trip to Great Britain

It may be of interest to some members of the Rubber Division to quote from a letter of June 27 from the Secretary of the Institution of the Rubber Industry to the Editor of Rubber Chemistry and Technology, in which reference was made to American rubber chemists and technologists who may visit Great Britain.

"If it could be arranged for any of your members who are making individual visits to this country to acquaint you or some official of the Rubber Division of this fact, in order that they could let me know when they would be coming over, it would enable us to meet them.

"Very often we hear that one or another of your members is over here just as he is about to leave.

"We are only too anxious to do whatever we can to repay in some small measure the hospitality that is invariably extended to our members when visiting you."

This is certainly a most cordial invitation, and it is hoped that some of our members may be able to take advantage of this sincere offer to add to their enjoyment and knowledge while they are in Great Britain. Those of the Division who have already been fortunate enough to visit Great Britain well know the hospitality and good fellowship which always await our members.

New Books and Other Publications

Handbuch der Gesamten Kautschuktechnologie. Handbook of Rubber Technology. Edited by E. A. Hauser, with the collaboration of prominent specialists at home and abroad. Berlin: Union Deutsche Verlagsgesellschaft, 1935. Vol. I, pp. xxiv + 1 - 834; Vol. II, pp. xiv + 835 - 1640. Price, 2 vols., bound in cloth, 280 Reichsmarks.

This latest addition to the list of those very unhandy "handbooks" that our German cousins delight in producing is no exception to the rule as regards bulk. It provides a good eight pounds avoirdupois of solid reading matter.

The aim of this monumental work is, in the words of its editor, to present a really comprehensive review of the technology and manufacture of rubber, covering every field in which this most versatile of materials is used. It is intended to serve both the layman, as a convenient reference book, and the rubber technologist as a source of detailed information on unfamiliar branches of the subject. Dr. Hauser has adopted the wise course of enlisting the services of several well-known experts—German, Austrian, American, British, and French—each of whom contributes one or more chapters on his own special subjects. Although this method results in some lack of uniformity and in a certain amount of overlapping, the advantages far outweigh any such defects, for it is probably true to say that no one man could write authoritatively on all the varied aspects of rubber technology covered by this handbook.

The names of the collaborators and the world-wide reputation of the Editor, Dr. Hauser, who himself contributes two chapters, including that on latex technology, are in themselves a guaranty of a high general standard.

In addition to the chapters dealing with specific types of rubber products, chapters are included on chemical testing and technical testing of rubber, rubber machinery, compounding technic and mixing methods, reclaim, factice, solvent recovery, latex, oxidation and aging of rubber, and rubber derivatives and synthetic rubber isomers. The chapters on rubber manufacture cover such varied articles as general mechanicals, tires, railway goods, automobile accessories, erasers, proofed fabrics, belting, balloon fabrics, leatherette, artificial velour, plasters, hollow goods, tennis balls, golf balls, toys, dipped goods, cut sheet goods, druggists' sundries, footwear, sponge rubber, flooring, paving, thread, packings, cables, hard rubber, rubber coverings for metals, brake linings, etc., dental rubber, and rubber-bonded abrasives.

It will be seen that the subject as a whole has been dealt with comprehensively. Moreover, the treatment within each individual chapter is, generally speaking, very thorough, covering every aspect of the subject under discussion from raw materials, mixings, processing, special machinery (general rubber-working machinery being left to the separate chapter on this subject), vulcanization, and finishing, up to the final testing of the product. As is perhaps inevitable under the system of collective authorship, the treatment is not equally thorough throughout; thus, some subjects, such as chemical testing, rubber machinery, compounding technic, tires, toys, and footwear, are dealt with in an exceptionally full and detailed manner, while in other cases, such as belting and leatherette, the treatment is briefer and more general. There is some lack of uniformity, also, regarding sub-headings and references to literature. Thus, while most chapters are sub-divided into numbered and headed sections, a few are devoid of this useful help. In many chapters copious references to literature are given in numbered footnotes, but in

others these are in the text, while some chapters contain practically no literature references at all. Incidentally, in a book containing so many references to patents, a patent index would be a useful addition.

A few items were noted, which seem rather scantily or inadequately treated; such are the testing of hard rubber and of reclaim, testing of vulcanized rubber for oil resistance, manufacture of airbags, vulcanization of flooring, and the testing and properties of belting. On the other hand, in the final chapter several pages are devoted to the chemistry of certain rubber derivatives which at present appear to have no technical importance. More information might with advantage have been given on the origin, properties, etc., of commercial types of raw rubber; thus, the index does not even mention crepe, smoked sheet, or Para.

The most noticeable omission in the subject matter is the electrodeposition (anode) process, which could not be traced either in the index or the text. A few well-known types of manufactured article (*e. g.*, fabric hot water bottles, molded bathing caps, and ebonite dust moldings) appear to receive no mention, and among miscellaneous minor omissions were noted the examination of fillers for grit, the Carius method of total sulfur estimation, the method of vulcanization of leatherette, the lead-sheath curing method for hose, the lead-sheathing process for cables, and the air-bomb and the dry and moist heat (Admiralty) accelerated aging tests.

In a book containing such a mass of detailed information it is not surprising to find a few errors or questionable statements. Thus, on pp. 107-8 reference is made to the "now generally adopted ring test-piece" (for tensile tests), and no reference is made to the types of dumb-bell test-piece now very generally used, or to the well-known Scott tensile tester. The chapter on thread contains (p. 1241) the curious statement that "testing in the Geer oven does not give satisfactory results, because . . . the action of air is excluded. On the other hand, an apparatus in which the action of light is fully excluded and only circulating air can act gives better results." Some of the physical properties of "rubber" quoted on p. 1338 need revision, notably, the cubical coefficient of expansion (0.00008) and the elastic modulus (26.3 kg./mm.²); again, on p. 1313 the breaking elongation of good quality ebonite is given as 1.5%, whereas it may be very much higher than this. The statements that all rubber vulcanizates are suitable for resisting coal gas (p. 1344), and that halogen compounds are solvents for vulcanized rubber (p. 1345) need modification. A minor error occurs in Fig. 197, where the hardness is given as "Shore" instead of "Plastometer."

It is almost inevitable that in a book composed of chapters written by several different authors there should be a certain amount of overlapping and duplication. Thus, we find abrasion testing dealt with both under "Technical Testing" and under "Compounding Technique;" influence of compounding ingredients on the properties of the vulcanizate under "Compounding Technique" and "Technical Rubber Goods;" and accelerated aging under "Chemical Testing" and "Oxidation and Aging of Rubber." Incidentally, the testing of aging properties, electrical properties, and light fastness would come more appropriately under "Technical Testing" than under "Chemical Testing," as at present. It is scarcely correct, moreover, to class fatigue, abrasion, and hardness tests under the heading "Elasticity," as is done in the chapter on Technical Testing.

A rearrangement of the chapters would in some cases make the sequence more logical; thus, "Hard Rubber" and "Dental Rubber" should be adjacent, as should also "High Pressure Packings," "Rubber in Frictional Elements" (brake linings, etc.), and "Rubber-Bonded Abrasives;" again, "Eraser Rubber" seems rather out

of place between "Rubber in Automobiles" and "Rubberized Fabrics," and "Thread" between "Rubber Paving" and "High Pressure Packings."

Another improvement that may be suggested is a more complete system of cross references from one chapter to another. The need for this is particularly noticeable in connection with latex processes, which are mainly grouped together in the latex chapter but are not always referred to in the chapter dealing with the particular article in question. The disposition of the matter dealing with latex could, in fact, be improved, as some processes are fully described in chapters other than that devoted specially to latex.

It must be understood that attention has been drawn to these minor defects not with any intention of conveying an adverse opinion of the book as a whole, but with a view to offering constructive suggestions that may prove helpful when a subsequent edition is prepared, as no doubt it will be in due course.

Considering the magnitude of the task they have undertaken, Dr. Hauser and his collaborators are to be congratulated on having so successfully carried this through, and thereby presented the industry with the most complete and detailed account of rubber technology that has yet appeared, and one that will undoubtedly remain for a long time to come the standard work on this subject.

In conclusion, it must be added that the paper, printing, illustrations, binding, and indeed the whole "get up" of these two imposing volumes are excellent. [J. R. Scott in the *India-Rubber Journal*.]

Twenty-sixth Report of the Rubber Growers' Association, Inc. Published by the Rubber Growers' Association, Inc., 19 Fenchurch Street, London, E. C. 3, England.

A report of activities and a statement of accounts for the year ending December 31, 1934, is contained in the 26th R. G. A. report. Brief mention is made of the progress of each of the Association's numerous committees in addition to specific mention of technical research and new product development conducted during the past year. A complete list of members, both company and individual, is also included. [From *The Rubber Age* of New York.]

Industrial Cable. Distributed by General Electric Company, Schenectady, New York. September, 1934. 128 pp.

Describing and listing all the standard types of insulated wire and cable that are used by industry for transmission, distribution, and control, this catalog, printed in clear, concise style, devotes an entire section to rubber-insulated cable. In this section is contained a summary of the types of cable available and recommended applications of each type. Results of tests, both physical and electrical, conducted on various types of rubber-insulated cable, are also given. [From *The Rubber Age* of New York.]

The Economic Characteristics of Rubber Tire Production. By Leonard E. Carlsmith. 230 pp. \$4.00.

(Available from the Book Department of *The Rubber Age*.)

Prepared and written in keeping with the requirements for the degree of Doctor of Philosophy, under the Joint Committee on Graduation Instruction, Columbia University, New York, this book records the results of an exhaustive study of the tire manufacturing industry in the United States. The author's purpose, and accomplishment, was to ascertain the nature of the more important economic characteristics of the industry, and where possible to measure them. Since graphic charts of these characteristics have been sadly lacking in the past the author was required to delve deeply into available information and construct his own graphs

and charts which are liberally used throughout the book. Because crude rubber is so intimately connected with the tire industry, both technically and economically, a chapter is devoted to it, including price fluctuations, supply and demand, statistics, and other variations. In his introduction the author candidly states that "the results of this research do not lead to a single conclusive proposition." Instead, he continues, there are presented "a number of derived relationships and trends... all varying in importance and significance." Because of the nature of this work only a limited supply of the books are available. Due to its combined value in presenting both theory and hitherto unpublished fact the book merits a place in rubber and rubber tire technical libraries. [From *The Rubber Age* of New York.]

Tyre Machinery. Francis Shaw & Co., Ltd., Corbett St. Ironworks, Manchester 11, England.

This catalog is released by an old-established (1879) machinery concern, which during the past fifteen years has been the only engineering firm in Europe to concentrate on the supply of completely equipped factories for tire building. The machinery line comprises mills, calenders, and a great variety of tire building machines and accessory equipment, tire fabric bias cutters, tubing machines, watchcase vulcanizers, hydraulic autoclave presses, temperature and time cycle control, as well as special machinery for the manufacture of all classes of rubber goods. All of this equipment is clearly illustrated and briefly described in English, French, and German. Every rubber engineer should keep a copy on file for reference. [From the *India Rubber World*.]

The Story of the Tire. Published by the Goodyear Tire & Rubber Company, Akron, Ohio. 48 pp.

With the statement that "the story of Goodyear is the story of the tire" Goodyear has published the fifth edition of this "story," the first of which was issued in 1922. The latest edition is a decided improvement over previous issues in style, make-up, and information. Concise description is made of rubber cultivation, fabric production, and tire and tube manufacture. Every step is well illustrated. Other chapters in the book are devoted to the wide variety of rubber products turned out by the Goodyear factories. The importance of rubber research and development is stressed. Brief biographies of the company's administrative officers are included. Dozens of Goodyear products, from tires to rubber bands, are illustrated. The book makes excellent reading for the rubber novice as well as for the rubber executive interested in learning of Goodyear's progress. [From *The Rubber Age* of New York.]

A Glossary of Terms for Rubber Manufacturers. Prepared and distributed by the Stamford Rubber Supply Company, Stamford, Connecticut. 32 pp.

One of the handiest "rubber dictionaries" to be presented in a long time is this glossary of terms relating to rubber, its uses, and manufacture. Practically all of the more common terms peculiar to rubber manufacturing will be found in this booklet as well as several not so well known. The booklet also embodies the advantages to be gained by the use of factice. It has been prepared, primarily, for the practical rubber worker. [From *The Rubber Age* of New York.]

Goodyear Motion Pictures. Distributed by the Goodyear Tire & Rubber Company, Akron, Ohio. 36 pp.

This catalog contains a complete list of the twenty-nine motion pictures prepared by Goodyear for showing at public and private functions. Each film available

is listed and sufficiently described. The films run from those depicting rubber cultivation in the Far East to action pictures of motorcycle races. No charge is involved to the exhibitor of these films. [From *The Rubber Age* of New York.]

Annual Survey of American Chemistry. Vol. IX. 1934. Edited by Clarence J. West. Published for The National Research Council by Reinhold Publishing Corp., 330 W. 42nd St., New York, N. Y., 1935. Cloth, 396 pages, 5½ by 8½ inches. Indexed. Price \$4.50.

This survey of chemical progress for 1934 follows the same general principles as preceding volumes except that the chapter on "Biochemistry" is omitted. Many of the topics which would normally appear in such a chapter are included in the chapters on "Food" and "Fermentation." Of the twenty-five chapters this year twelve are devoted to industrial topics. An important feature of these chapters is that they suggest trends in the industry as well as present the accomplishments of the period covered.

In the chapter on rubber H. L. Trumbull, research chemist of The B. F. Goodrich Co., Akron, O., reviews chemical progress in that industry by topics in the following order: crude rubber, rubber hydrocarbon, vulcanization and the structure of rubber, accelerators of vulcanization, age-resistors, control and testing, pigments, compounding ingredients, cements and adhesives, rubber technology, latex and rubber dispersions, synthetic rubber and rubber-like products, derivatives of rubber.

In the chapter on "Textile Chemistry" references are made to the industrial uses of rubber latex, lacteron and Lastex, and Duprene as applied to textiles. [From the *India Rubber World*.]

The Elasticity of Rubber

Kurt H. Meyer and Cesare Ferri

LABORATORY OF INORGANIC AND ORGANIC CHEMISTRY, UNIVERSITY OF GENEVA, SWITZERLAND

In order to explain the elasticity of rubber, several authors assume that long chain molecules have a tendency to form spirals, and that when an external force displaces them from this state of equilibrium, they tend to return to it. These concepts lead in turn to two different points of view.

1. It may be assumed that there are forces of attraction between the different parts of a single molecule, for example, between the double bonds. Upon stretching, these forces of attraction are overcome. The free energy of the stretched thread thus consists of the potential energy of the molecular parts which have been separated from one another.

2. On the other hand, the molecule may be said to have a certain rigidity which, in its final analysis, depends upon the rigidity of the tetrahedric valences of carbon. In this case it is to be assumed that stretching brings about a deformation of the angles between these vectors.

The first hypothesis has been developed by several authors.¹ Recently Mack² has assumed that there are forces of attraction between the hydrogen atoms in the rubber chains. He attributes the phenomena of elasticity to a mechanism of "evaporation and condensation of hydrogen."

None of these hypotheses explains the elastic properties which are found in substances such as elastic ligaments, and especially in elastic sulfur,³ which have a wholly different structure from that of rubber. Moreover these two hypotheses, which involve a change in the total potential energy, are incompatible with the fact that the tension of substances such as rubber, which are stretched and held at a constant length, increases with the temperature. Now a rise of temperature ought to diminish the work necessary to overcome on the one hand the forces of attraction and on the other hand the forces which keep the atoms in a position of established equilibrium. The result would be that the tension of a stretched rubber thread would diminish with an increase in temperature.

On an entirely different basis, Meyer, von Susich, and Valko⁴ have proposed a kinetic theory of elasticity from which we quote the following conclusions.

The principal valence chains are oriented by stretching. Consequently, in the direction of stretching the atoms are held together by homopolar bonds of great stability, to which corresponds a very low heat content, comparable to that of the bonds of diamond. The greater part of the heat content originates in transverse movements, for example, in movements of rotation which are complete or incomplete about the direction of the chain, and which may be compared to a vibrating cord. These movements cause a pressure perpendicular to the direction of stretching, a pressure which is equivalent to a tension in the direction of stretching.

Busse⁵ proposed a similar theory at almost the same time.

In the present work we have tried to throw light on the problem by following the thermodynamic method.

1. Thermodynamic Investigations on Rubber

The well-known fact that stretched rubber possesses a negative linear coefficient in the direction of elongation has already been the object of several thermodynamic

investigations. Thermodynamics requires that such a body should liberate heat upon stretching. This liberation of heat during deformation has been known for a long time under the name of the Gough-Joule effect. This has been studied in detail by Hock,* who was able to show that the liberation of heat during complete extension of unvulcanized rubber reaches approximately ten calories per gram. This quantity is a multiple of the energy which appears in the form of work during stretching of the system. Hock laid emphasis upon the diminution of the total energy during stretching to high elongations, and as early as 1922 concluded that this phenomenon is to be interpreted as a liberation of the latent heat of fusion. Under the influence of traction, the molecules are oriented and arrange themselves in a regular network, with liberation of the heat of fusion. This hypothesis was later confirmed by Katz, who proved that unvulcanized rubber forms a fiber diagram when it is stretched. For this reason stretched rubber is usually described as "crystallized" or "crystalline."

Because of the use of the word "crystalline" we consider it pertinent to make the following observations. In certain regions the atoms of stretched rubber form a tridimensional network. These crystalline regions are not large, and their dimensions are still beyond the visible range⁷ (approximately $500 \times 150 \times >600$ A.). It has been proved that there is liberation of a definite quantity of heat (10 calories per gram) at the time of the formation of these crystallites, which is of the same order of magnitude as the heat of fusion of a large number of organic compounds. This would appear to warrant the designation "crystalline" for the state of rubber when stretched.

In his later studies, Hock has been occupied with this crystallization and with other types of aggregation, but he has not concerned himself particularly with the mechanism of contraction.

In a recent work, Ornstein, Wouda, and Eymers⁸ studied the thermodynamics of rubber. They investigated the decrease in temperature during adiabatic stretching, and studied the following equation:

$$\Delta T = T \int_0^{\Delta l} \frac{\left(\frac{\delta S}{\delta l}\right)_T \left(\frac{\delta l}{\delta T}\right)_S}{\left(\frac{\delta \epsilon}{\delta T}\right)_l} dl$$

where T represents the absolute temperature, $\left(\frac{\delta S}{\delta l}\right)_T$ the modulus of elasticity

at constant temperature, $\left(\frac{\delta l}{\delta T}\right)_S$ the coefficient of linear dilation at constant ten-

sion, and $\left(\frac{\delta \epsilon}{\delta T}\right)_l$ the specific heat at constant length. The aim of their work was

to verify this formula. They found experimental values which agreed with those calculated by the preceding formula up to an elongation of 150 per cent; above this limit there was no longer agreement. The authors attribute this to the influence of a second phase, which is formed above a certain elongation. We do not believe that this is a satisfactory explanation of the difference between the observed and the calculated values. The theory must remain valid, even if several phases coexist. It would, on the other hand, be invalid if irreversible phenomena play a part, as for example, a permanent elongation or if equilibrium has not had time to become established. In our opinion, this offers an explanation of the variations between the theoretical and experimental results.

2. Apparatus and Experimental Method

Conforming to the aim of our investigation, we attempted to measure the thermal coefficient of the elastic force exerted by rubber stretched to a constant length,⁹ after elimination of the irreversible phenomena.

The apparatus most suited to measurements of this type is the dynamometer of Polanyi,¹⁰ which we adapted to our purpose.¹¹

Figure 1 shows the arrangement and the principle of the operation of this apparatus. A sturdy metal frame which can be lengthened by a sliding bar carries on its upper part two knife blades, K, 42 millimeters apart. On these two knife blades rests horizontally a steel spring R, and this has two small vertical mirrors

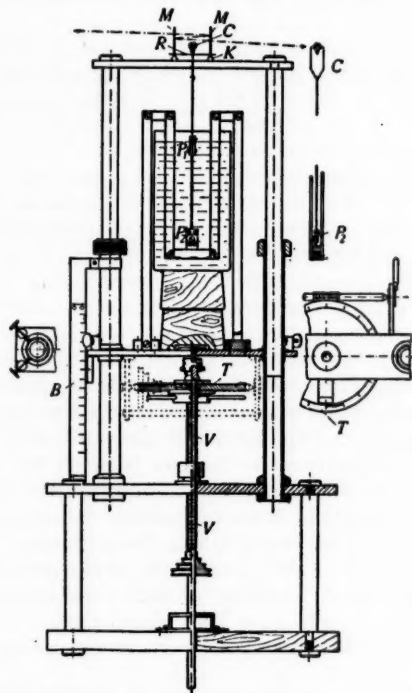


Figure 1—Polanyi Dynamometer

M (13×35 mm.) attached by wax facing one another. A clamp P_1 holding the upper end of the strip to be studied is suspended by a rigid hook to the middle of the spring by means of a staple C. The lower end of the strip is held by another clamp P_2 in the vertical movement, controlled by a micrometric screw V. All rotation of this second clamp is prevented by the metal guide with which it is equipped, and which slides on the lateral columns of the frame. The strip is immersed in a vessel filled with water, which makes it possible to keep the strip at a constant temperature. It is evident that the micrometric screw and the guide should move with very little friction and with the least possible play. All portions of the apparatus, with the exception of the spring, should be perfectly rigid and incapable of deformation.

When the two clamps are moved away from one another, the spring bends as soon as the strip begins to be stretched, and this bending permits the measurement of the force acting on the spring. In order to measure this force, the image of an illuminated vertical scale, placed several meters distant from the apparatus and reflected successively in the two mirrors, is observed through a glass with horizontal cross hairs, placed on the other side of the apparatus. Every bend of the spring brings about a displacement of the image of the scale, and this displacement depends upon the distance between the scale and the glass. The maximum bend corresponds to one millimeter of actual lowering of the center of the spring, resulting in an apparent displacement of 500 millimeters of the image of the sample in the glass. This makes it easy to estimate 0.0004 of the maximum force which can be exerted on the spring. The apparatus is equipped with several interchangeable springs.

The elongation of the object examined is measured in millimeters by means of the graduated bar B, placed on the side of one of the columns of the frame, and in fractions of millimeters by means of the disc T of the micrometric screw. Since the pitch of the screw is 0.5 millimeter, 0.001 millimeter, which corresponds to 0.002 of a turn, can be estimated easily.

The calibration of the apparatus is carried out in two steps. A series of weights is suspended from the hook of the spring, and the apparent displacements on the scale are read in the glass. A completely rigid and inextensible object, *e. g.*, a strip of steel, is then fastened between the two clamps, and there is read by the glass the displacement of the image on the scale corresponding to the lowering of the center of the spring, which is measured by means of the micrometric screw. This measurement serves to correct the elongation determined by the displacement of the micrometric screw to a fraction of a millimeter, by which the center of the spring is lowered by the traction exerted. In order to measure the initial length of the strip of rubber, the point where the two clamps touch is first measured, then the clamps are separated, and the tension is observed every 0.1 millimeter. By means of a graphic interpolation the distance between the clamps at which the strip of rubber commences to be stretched can be measured exactly. For measurements of very great elongations with very elastic substances, more particularly with vulcanized rubber, it is necessary to take the precaution of fastening the strip in the clamps under tension. If this is not done, at elongations above 200 per cent the rubber slips in the clamp, especially at high temperatures, and this happens even if the screws of the clamp have been closed firmly. This slipping renders all the measurements void, and caused us much annoyance at the beginning of our tests.

For measurements at different temperatures we made use of an apparatus which furnished a current of water from 200 cubic centimeters to 1 liter per minute at a temperature varying from 12° to 80° C., and constant within 0.5° C. This apparatus allowed us to pass from high temperatures to lower temperatures in two minutes. The passage in the other direction, *i. e.*, to higher temperatures, was a little slower. In order to reach lower temperatures the work was carried out with a mixture of methyl alcohol and carbon dioxide snow.

3. The Irreversible Phenomenon of Relaxation

When stretched energetically, rubber shows the phenomenon of relaxation *i. e.*, its tension diminishes with time. Since this phenomenon is partially reversible, and we wished to study reversible transformations, we were obliged to measure the relaxation and to exclude it. Relaxation is most easily observed when rubber that has not been vulcanized is stretched. Its tension diminishes to almost zero

if the work is carried out at 60° C. It can then be stretched again and the process repeated. The curves which have been published by Hauser¹² represent this behavior in a particularly clear manner. This leads to the belief that the principal valence chains, which are first oriented by stretching, begin to slide in such a way that their component parts ultimately occupy a chaotic arrangement of the maximum probability. Unvulcanized rubber, after complete rest, again becomes isotropic. The final result is thus equal to an irreversible deformation, so that rubber behaves like a very viscous fluid.

The effect of vulcanization is to limit the relaxation, *i. e.*, there is practically no diminution in the tension beyond a certain value. We were thus forced to use for our experiments a rubber the relaxation of which stopped in a relatively short time.

As a result of experiments with different types of vulcanized rubber, two samples having properties particularly favorable were selected for our experiments. Professor van Rossem of Delft very kindly had them prepared for us.

The samples had the following compositions.

Rubber No. 1	
First latex crepe	100 parts
Sulfur	8
Vulcanized 3 hours in an autoclave at 147° C. Sample 5 mm. thick.	

Rubber No. 2	
First latex crepe	100 parts
Zinc oxide	3
Sulfur	5
Diphenylguanidine	1
Vulcanized 30 minutes in an autoclave at 147° C. Sample 0.6 mm. thick.	

Rubber No. 1 was cut into pieces $1.2 \times 5 \times 40$ millimeters, and pieces $0.6 \times 5 \times 40$ millimeters were died out of rubber No. 2. The test pieces were fastened in the jaws of clamps in such a way that the length of the rubber which was stretched was approximately 12 millimeters.

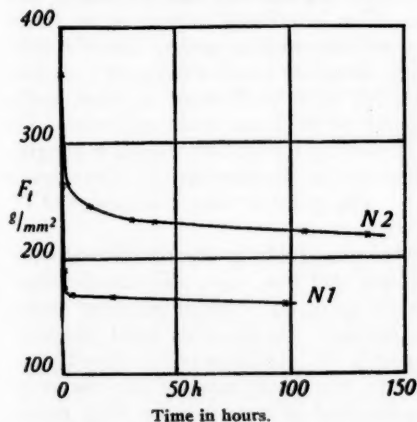


Figure 2—Relaxation of Rubber

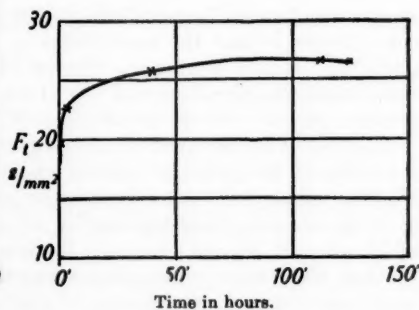


Figure 3

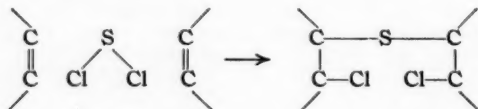
Since relaxation is much more rapid at elevated temperatures, in all cases the samples of rubber were exposed for a sufficiently long time at the highest temperature to be used during the measurements, and were stretched in this condition. We then waited until the tension remained practically constant. In this way it

was possible to determine the tension at lower temperatures, and to determine the original tension when after several hours the initial temperature was reached.

When a piece of rubber, which has first been stretched energetically and which after relaxation is still under considerable tension, is allowed to contract by diminishing the length, and if the smaller tension which then exists is measured, it is found that this tension increases with time. Figure 2 shows the course of tension F_t at a deformation of 400 per cent elongation, and the temperature constants for the two formulas. Figure 3 represents the increase in the tension of rubber No. 2 after a rapid release, which lowered the elongation of 400 per cent to 50 per cent.

The phenomena of limited relaxation and of slow contraction may be explained on the basis of the molecular constitution of rubber when certain hypotheses regarding the mechanism of vulcanization are assumed.

Weber¹³ earlier believed that during vulcanization sulfur reacts with two double bonds. One of us¹⁴ has succeeded in confirming this hypothesis for cold vulcanization. From these experiments it was found that two double bonds—in general the double bonds of two different chains, situated side by side—enter into reaction according to the scheme:



Tests on the hot vulcanization of rubber which have recently been made by Hohenemser of this laboratory lead to a similar mechanism for the reaction.

Starting from this purely chemical point of view, these concepts have been transposed by Meyer and Mark¹⁵ to a morphological basis. The rubber molecules are considered to be long flexible fibers, held together by sulfur bridges, thus forming an irregular reticular structure. This interlaced system is no longer soluble in organic solvents, but still has a certain swelling power. On the other hand, the possibility of the molecules sliding along one another is less or even non-existent. At higher degrees of vulcanization more and more of these sulfur bridges are formed between two double bonds of the same chain molecule. The consequence is that the possibilities of stretching the rubber diminish progressively and finally disappear. Similar ideas on the mechanism of vulcanization were announced simultaneously by Hock.¹⁶ This point of view is accepted at the present time by several investigators.¹⁷

The type of rubber used by us was not wholly insoluble in organic solvents, and a portion of the principal valence chains was still free, *i. e.*, still unvulcanized. Slightly vulcanized rubber is therefore made up of an irregular reticular system of chains of rubber held together by sulfur bridges. On the other hand, molecules which are still free are present in the interior of this structure of low density.

When the rubber is stretched energetically, the whole mass of the chains become oriented, *i. e.*, the chains of the vulcanized system because they cannot behave otherwise than as a fiber which undergoes traction in a given direction, and the other chains because of friction which entrains them. Although the former are fixed in their positions, the latter type of chains can begin to move, slide, and again reach a chaotic orientation, such as is present in amorphous unstretched rubber. For this reason the tension diminishes from the value which is characteristic of free unvulcanized chains.

The vulcanized system contracts as soon as the traction is no longer applied. Entrained by the friction, the system of unvulcanized chains will be compressed in the direction of the release. The result of this is apparently an initial state of equilibrium between the tendency of the vulcanized system to contract and the tendency of the unvulcanized system to expand. The latter system, the molecules of which are able to slide, will not remain in its original position. The tendency of the first system to contract will again become manifest, and following this the tension of the rubber increases or rather, if all tension is avoided, the rubber contracts slowly.

4. Tests at Small Deformations

A Comparison between the Coefficients of Tension and of Compression.—The thermal coefficient of tension is negative for small elongations up to about 10 per

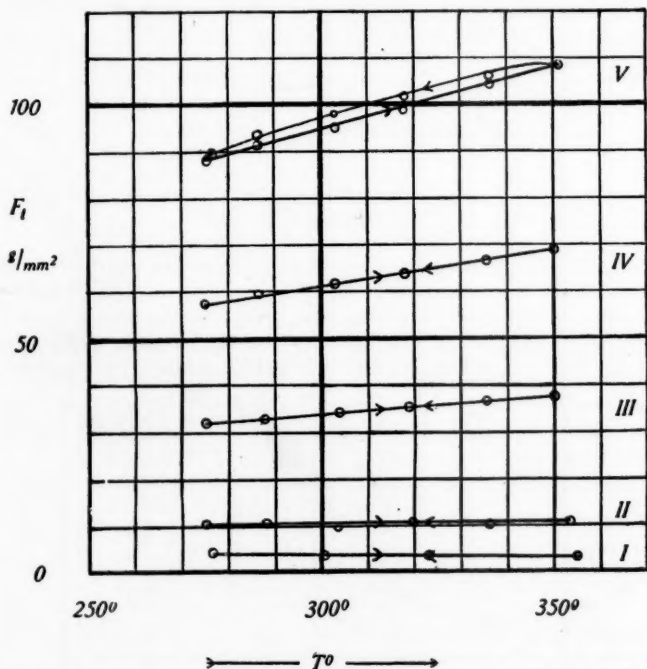


Figure 4—Sample No. 2. Elongation: I, 4%; II, 11%; III, 33%; IV, 77%; V, 166% (See Note 18)

cent. Rubber then behaves like an ordinary substance, with a positive coefficient of dilation. At an elongation of about 10 per cent, the tension is found to be independent of the temperature, that is, the coefficient of linear dilation in the direction of stretching is equal to zero. At higher deformations, the tension increases with the temperature, which indicates a negative linear coefficient of dilation. In this way two effects are in conflict with one another, *i. e.*, the ordinary thermal dilation of a solid substance, and the special property of stretched rubber to contract when the temperature rises. These two phenomena compensate each other when the elongation is about 10 per cent. Figure 4 shows this behavior. The theory of the superposition of these two phenomena is confirmed by a com-

parison of the thermal coefficients of tension of stretched rubber and the thermal coefficients of pressure of compressed rubber. In the latter case, the coefficient of pressure and of ordinary dilation act in the same sense, *i. e.*, the two effects are additive. We believe we have approached sufficiently well the precise value of

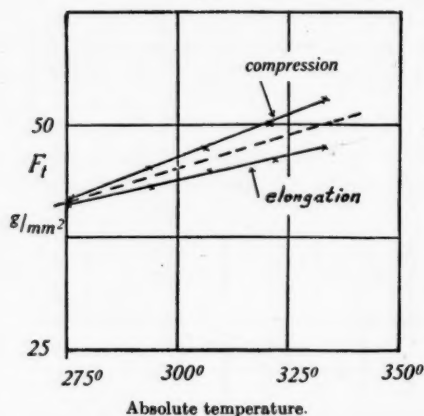


Figure 5

the elastic coefficient by taking the average value of the thermal coefficients of tension and of compression. This is equal to an increase in the tension of about 0.05 gram per square millimeter per degree. Figure 5 represents the tension and the compression of sample No. 1 as a function of the absolute temperature. The dotted line represents the average of the two values at the same temperature.

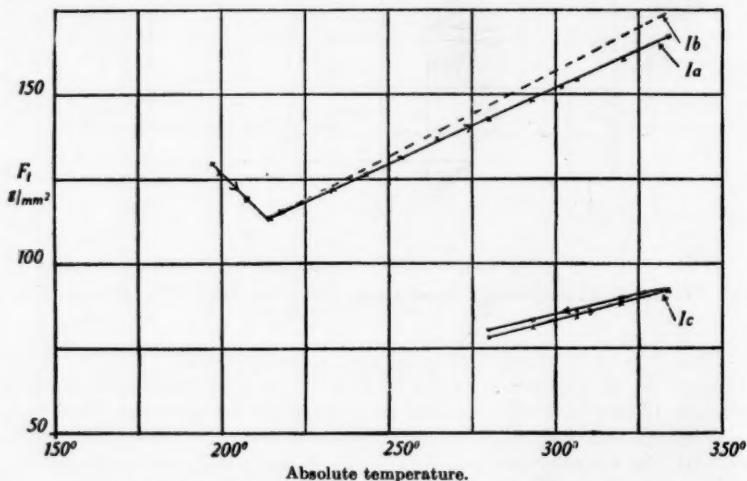


Figure 6—Elongation: 1a, 35%; 1b, 35% Corrected; 1c, 170%.

We have limited ourselves to a determination of the thermal coefficient of tension, to which we have added the correction mentioned above.

The same result can be reached by the following method, *viz.*, to determine the

corrected thermal coefficient the operation should be made, not at a constant length, but at a constant deformation. At a higher temperature, it would, in this case, be necessary to use a length which can be calculated by means of the linear coefficient of dilation of the unstretched rubber. This would involve the same correction.

5. Experiments with Rubber No. 1

Figure 6 represents the tension of sample No. 1 as a function of the absolute temperature at two deformations, *viz.*, elongations of 170 per cent and of 350 per cent. Figure 6 and Table I show that tension F_l is a linear function of temperature T in the region of -50° to $+70^\circ$ C., and it becomes proportional to it when the slight correction Δ which has just been discussed is made (dotted curve).

In interpreting this, we have not taken into consideration the complications arising from the formation of a crystalline phase. X-ray control has shown that rubber No. 1 at ordinary temperature, and even at 400 per cent elongation, does not exhibit any crystalline interference. The diagram which is obtained consists only of a delicate ring, the intensity of which is at its maximum at the height of the equator.

The thermal coefficient changes its sign below a temperature of -50° C. Below this temperature the rubber has lost its characteristic elasticity. It has become hard, and from the point of view of the thermal coefficient of tension it behaves in this region like an ordinary solid substance.

6. Experiments with Rubber No. 2

Rubber No. 2 has more complicated properties. Nevertheless within certain limits of temperature and tension, the same relation is found between the tension and the absolute temperature as in the preceding case. This behavior is shown in Fig. 4, Curves IV and V. Below 20° C. the curve has a greater slope, and the thermal coefficient of tension increases instead of remaining constant. When stretching is increased to 400 per cent, this anomaly is found at all the temperatures tried in our experiments. This anomaly, to which we shall return later, is in our opinion attributable to a phenomenon of crystallization, which is revealed by x-ray.

This crystallization was not observed under the same conditions as with rubber No. 1, and therefore the reason must be sought in the higher content of sulfur, the action of which consists in a lowering of the point of crystallization, either by acting in the free form as a simple diluent or else in the combined form, where it leads to a more irregular structure.

7. Theoretical Results

If the work against atmospheric pressure, which is negligible in respect to the energy which plays a part, is disregarded and if one considers only transformations which are completely reversible, there results from the proportionality between the tension and the temperature the following relation:

$$-\left(\frac{dF_l}{dT}\right)_l = \left(\frac{dS}{dl}\right)_T = \frac{1}{T} \left(\frac{dQ}{dl}\right)_T \quad (1)$$

where F_l = the force per square centimeter of the original cross section (section of rubber before stretching)

S = entropy

Q = quantity of heat absorbed

l = length of the rubber sample.

Experimentally we have found

$$F_l = cT$$

where c is a constant. It then follows that

$$\frac{-dcT}{dT} = -c = \frac{1}{T} \left(\frac{dQ}{dl} \right)_T = \left(\frac{dS}{dl} \right)_T \quad (2)$$

$$-cT = \left(\frac{dQ}{dl} \right)_T$$

$$-F_l = \left(\frac{dQ}{dl} \right)_T; \quad -F_l \times dl = dQ \quad (3)$$

The product, $-F_l \times dl$, represents the work done during contraction, and Equation 3 shows that the work is equal to the quantity of heat absorbed. During this contraction there is, therefore, no change in the internal energy.

From the point of view of the kinetic theory of heat, this means that the potential energy is not altered by contraction. There are therefore no forces of attraction which are saturated, nor any angles of deformed valences which return to their position of equilibrium.

The nature of the mechanism of contraction is expressed by Equation 2.

$$-c = \left(\frac{dS}{dl} \right)_T$$

This equation shows that the entropy varies in the opposite sense to the length. On the other hand, the expression:

$$S = R \ln w$$

connects the entropy with the thermodynamic probability w , *i. e.*, during stretching the molecules or their component parts orient themselves in an arrangement of the least probability. In fact in amorphous rubber all positions are available for the different parts of the molecules, and the directions of valences C—C are distributed in a homogeneous manner in all directions of space. The deformation, as a result of stretching, causes an orientation of the principal valences in the direction of stretching, and therefore an arrangement which admits of a smaller number of realizations. When the external force no longer acts, the thermal movements bring about a return to the initial chaotic state, where all the positions are realized. This necessarily involves a contraction in the direction of stretching if the structure prevents slipping of the molecules.

Under the isothermic condition, the work done by the deformed rubber in its contraction can be compared with the work of expansion of an ideal gas, *i. e.*, in both cases the work is performed without a change in the internal energy at the expense of the heat which is absorbed.

Our results confirm and define the kinetic theory of elasticity which we quoted earlier.¹⁹

8. Experiments with High Degrees of Stretching

When stretching rubber No. 2 to 400 per cent, the curve representing the tension as a function of the temperature which is obtained differs markedly from those curves discussed above. If the work is commenced at 70° C. and the temperature is lowered, it is found that the tension at first diminishes in proportion to the absolute temperature, as in the case of small extensions. However, the tension

diminishes more and more if the temperature is kept constant for a certain time. If the temperature is again raised, the increase in tension is much more rapid than before, and this new curve joins the descending curve again around 70° C. The process is therefore reversible, and there has been no permanent

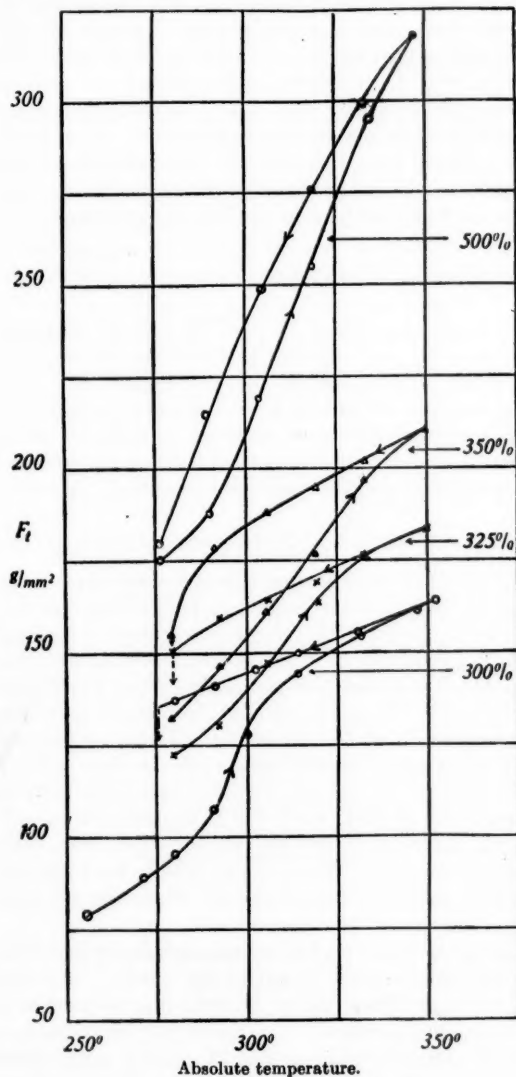


Figure 7

deformation. This behavior is illustrated in Fig. 7, where the cycles at different elongations are represented.

Here we are dealing with a phenomenon of the crystallization of deformed rubber. The chains of isoprene arrange themselves in tridimensional microcrystallites,

a process which takes place relatively slowly. The result is that when rubber is again cooled rapidly in such a way that the tension remains proportional to the absolute temperature, we have superfused rubber, with the same characteristics as rubber No. 1, which does not crystallize at all. Nevertheless, rubber No. 2 crystallizes very slowly under the conditions of the experiment, and its tension diminishes in consequence. When a similar piece of partially crystallized rubber is again heated, the increase in tension will be much more rapid because of the fact that the portion "in fusion" takes part in the tension.

It has been known for a long time that such a piece of rubber gives off heat when it is stretched. Hock in particular has emphasized the fact that this heat of crystallization may greatly exceed the quantity of energy absorbed in the form of work. In the latter case, there is at the same time a diminution of the entropy and a diminution of the internal energy, as a result of elongation by tension.

Consequently the contraction is accompanied by an increase in the internal energy, and this excludes the intervention of forces of attraction as a cause of the contraction.

It has been seen above that, from the point of view of thermodynamics, amorphous rubber behaves like a perfect gas, *i. e.*, it can perform work only by a change in the entropy without any change in the internal energy. In a similar way, partially crystallized rubber can be compared to a true gas or to a substance which evaporates. In this case, rubber upon contracting performs work as a result of a change in the entropy, and at the same time there is an increase in the internal energy, as during evaporation against external pressure.

9. Tests at Low Temperature. The Influence of Delayed Crystallization

The behavior of sample No. 2 is comparable at low temperatures and low elongations to the properties of this same sample at high elongations at ordinary temperature. Upon cooling below 0° C. a superfused state is reached, in which the tension diminishes in proportion to the absolute temperature. Subsequently the force continues to decrease at constant temperature (see Fig. 7, dotted lines). If the sample is now heated, the initial value of the tension is reached according to a curve which is very steep at the beginning. At low temperatures, especially typical phenomena of retarded crystallization can be observed. We have found frequently that the tension of a sample of rubber which has been energetically re-chilled increases regularly at first, when the temperature is raised. This normal behavior is suddenly interrupted and the tension diminishes, although the temperature continues to increase. Without any doubt, we have here a case of retarded crystallization, which is manifest only when the temperature has been raised sufficiently.

Everything leads to the belief that these retardations in crystallization are likewise the cause of a phenomenon observed by LeBlanc and Kröger.²⁰ These authors found that unvulcanized rubber, after having been stretched at -50° C. contracts at the same temperature. On the other hand, a sample of rubber stretched at -30° C. contracts only at +10° C., and a sample stretched at 0° C. shows the same phenomenon only at +20° C. The retardation is so pronounced at -50° C. that no appreciable crystallization can manifest itself if the rubber is stretched at this temperature. At higher temperatures, for example at 0° C., the retardation of crystallization is less, and the rubber crystallizes much more easily when it is stretched, so that it is necessary to heat it to the "fusion" temperature in order to bring about contraction.

10. Thermal Coefficient of the Tension of Rubber at High Elongations

When unvulcanized rubber is stretched in a particularly energetic manner, there is a very pronounced orientation and also a crystallization of a large portion of the rubber, as is shown in x-ray diagrams. A sheet of rubber thus obtained was vulcanized by exposure to sulfur chloride vapor. The product no longer contracted.

Figure 8, Curve 1, shows the behavior as a function of the time of this sample (very rigid) for elongations of 2 to 3 per cent; the tension was about 240 grams per square millimeters. When the temperature is raised, the tension diminishes. The characteristic of this product is thus entirely unlike that of rubber vulcanized by the ordinary method. Contraction is accompanied by a diminution in the internal energy.

The x-ray diagram of this sample showed that the principal valence chains

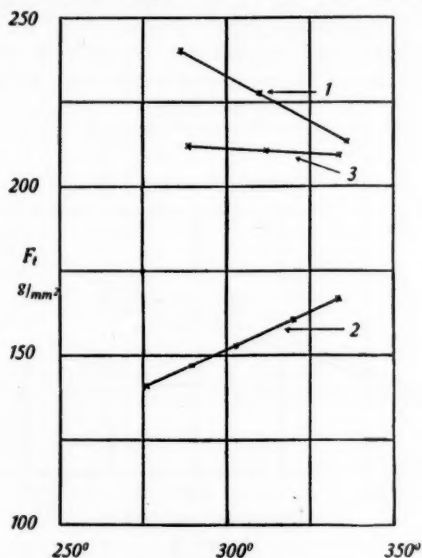


Figure 8

1. Vulcanized rubber under tension (2.7% elongation).
2. Rubber No. 1 (elongation 350%)
3. Steel spring (elongation 50%)

are already completely oriented. It is therefore no longer possible to influence this orientation by stretching. This deformation can affect only the tetrahedral angle between the carbon valences up to rupture of the sample. Upon deformation of the tetrahedral angles, the potential energy is increased, and when the external force is reduced to zero, the deformed angles resume their normal size. The behavior is comparable to that of an ordinary polycrystalline substance, for example, a steel spring. In Fig. 8, Curve 3, the tension-temperature curve of such a spring is compared with curves of vulcanized rubber in the stretched state (Curve No. 1) and of normal rubber (Curve No. 2) at mean elongation.

It is of interest to mention that Weise²¹ found a modulus of elasticity for rubber which increased from a value of two to the order of 1000 at high elongations, a figure which is of the order of magnitude of that observed with cellulose fibers and other substances composed of chains of primary valences in parallel orientation.

The effect of the deformation of the valences should also be manifest in smaller deformations than those we have observed, but in this case only by a slight change in the thermal coefficient of tension.

In short, we find therefore that there are four effects which govern the thermal coefficient of the tension at constant length. With the exception of irreversible relaxation they are:

1. A tendency to disorientation.
2. Thermal dilation.
3. Deformation of the valences.
4. Crystallization (aggregation).

The influence of the fourth factor can be eliminated by selecting a suitable type of rubber. The effect of factor No. 1 is responsible for the proportionality between the tension and the absolute temperature. Factors 2 and 3 have a common cause, but it is useful to consider them separately. Dilation (2) diminishes the tension upon stretching, but increases the resistance to pressure when the temperature is

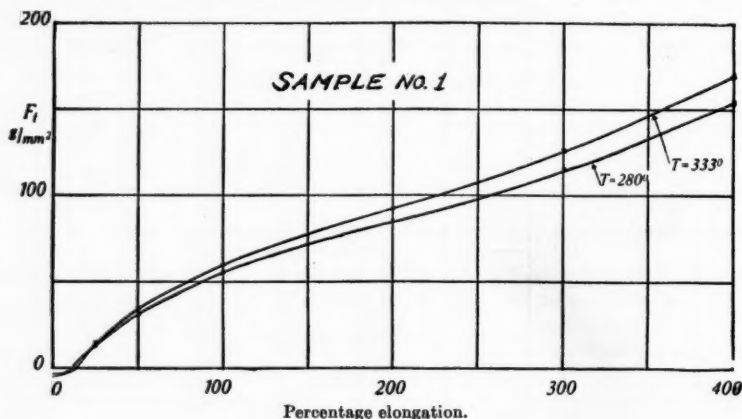


Figure 9

raised. The third factor manifests itself only at very high tensions, and when the temperature is raised, this factor lowers the force which is created when the rubber is stretched or when it is compressed.

The influence of factor No. 1 is superposed on factors 2 and 3. Factor 2 is most noticeable at low deformations, factor 3, on the contrary, at high deformations. The consequence is that the influence of factor No. 1 passes through a maximum at medium deformations. The maximum of the thermal coefficient of the tension corresponds to this maximum.

11. The Tension-Deformation Curve

In order to complete our data, we have shown in Figs. 9 and 10 the curves which relate the tension to the deformation, such as are obtained with the Polanyi apparatus. These curves are of too complicated a character for one to be able to deduce a simple relation between the force and the deformation, a relation which would be comparable to the $P \times V$ curve of a perfect gas.

The curves of the extension and contraction of sample No. 1 coincide. This is the case likewise with the corresponding curves of sample No. 2 obtained at

higher temperatures. However, at lower temperatures (Curve No. 0) the curves of extension and of contraction of sample No. 2 spread apart. This spreading apart is caused by the retardation of crystallization.

12. Tension and Internal Pressure

After elongation the highly stretched rubber exerts a force of 100 kilograms per square centimeter (based on the original cross section). Since the elongation is about ten times the initial length, the cross section is one-tenth of the original cross section. The tension of the rubber increases under these conditions to about 1000 kilograms per square centimeter, based on the cross section at the time. The tension may be replaced by a lateral pressure of the same size, *i. e.*, about 1000 atmospheres. In our opinion, in oriented rubber the heat content is represented for the most part by movements in a plane normal to the direction of elongation.

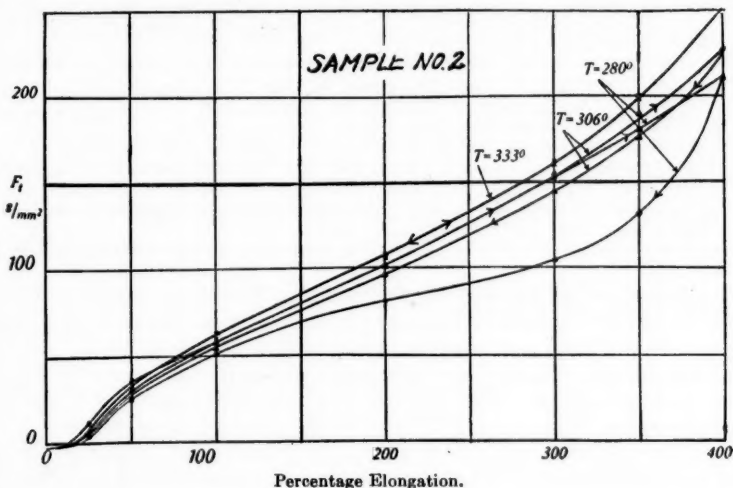


Figure 10

In other words, the greater part of the "thermal pressure" (internal pressure) is manifest in this repulsion. It happens that the value we have indicated, *viz.*, 1000 atmospheres, is of the same order of magnitude as that which has been found for the internal pressure of liquid hydrocarbons. This confirms our point of view.

Résumé

1. The tension of stretched rubber was studied as a function of the temperature.
2. The tension of a rubber containing 8 per cent sulfur, which shows no crystallization interferences when it is stretched, increases in direct proportion to the absolute temperature. It may be concluded that the work of stretching is transformed quantitatively into heat, whereas the work performed by contraction is drawn in the form of heat from the surrounding medium. There is no change of energy, involving for instance a saturation of the double bonds or the establishment of angles of deformed valences.
3. Contraction originates in an orientation of the polyprene chains by traction. Opposed to this orientation are thermal movements, which ultimately bring about a return of the oriented chains to disordered positions (variation of entropy).

4. Rubber which contains less sulfur has more complicated properties, as a result of a partial dissociation, which brings about crystalline properties during stretching. The influence of this phenomenon on the thermal coefficient of tension is discussed.

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- ¹⁸ Elongation based on the length of the sample at zero tension measured after having been tested.
- ¹⁹ Page 319.
- ²⁰ Memmler, "Handbuch der Kautschukwissenschaft," p. 481.
- ²¹ Weise, *Kautschuk*, **8**, 106 (1932).

Research on Modified Rubbers

Part VI. The Oxidation of Rubber Solutions with Gaseous Oxygen in Presence of Catalysts*

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In a previous study of the oxidation of rubber, the oxidative action of peracetic acid, or mixtures behaving substantially as such, was examined (Bloomfield and Farmer, *J. Soc. Chem. Ind.*, 53, 121T(1934)). The results then obtained pointed to a course of reaction characterized by (a) additive attack at the unsaturated centers of the rubber molecules, resulting in the production of a high degree of hydroxylation, and (b) extensive molecular degradation with liberation of carbon dioxide (see also Mair and Todd, *J. Chem. Soc.*, 1932, 386).

In an extension of this work, attempts have been made to prepare peracetic acid by means other than the interaction of hydrogen peroxide with acetic acid or anhydride, and among other methods the autoxidation of acetaldehyde at low temperatures in the presence of cobalt acetate as catalyst (G.P. 269,937; U.S.P. 1,179,421) was tried. Though peracetic acid was successfully obtained in this way in fair yield, an attempt to prepare it on a larger scale resulted in a violent explosion. In order to eliminate the danger arising from an accumulation of peracetic acid, oxygen was led into a chloroform solution of rubber containing a cobalt acetate catalyst together with acetaldehyde, with the hope that in this way peracetic acid might be formed *in situ*; at low temperatures (-20° to 0°) no reaction occurred, but on submitting such a solution to the action of oxygen at temperatures above 30° a very rapid reduction of viscosity set in, and the solution yielded a viscous gum containing a little oxygen. Now Stevens and his co-workers have recently shown that rubber solutions readily undergo oxidation by gaseous oxygen when certain catalysts (notably the heavy metal salts of organic acids) are present. It immediately became apparent that the oxidation phenomenon just described affords the basis for a greatly accelerated process of this type, the acceleration being due to the presence of acetaldehyde. It was thought desirable at this stage to investigate broadly the entire subject of oxidation of rubber solutions in the presence of catalysts of this nature, and a study has accordingly been made of the oxygen absorption of rubber solutions containing different catalysts, the oxygen intake being measured by the contraction occurring in a closed system containing oxygen, the latter being kept constantly circulating by means of a pump of the pattern designed by Finch (*J. Chem. Soc.*, 1925, 2464). Since it was found that a considerable quantity of carbon dioxide was formed during oxidations of this type, the circulating gases were passed through a trap containing baryta water, and at any stage of the oxidation the amount of carbon dioxide formed could be ascertained by removing the contents of the trap, filtering off the precipitated barium carbonate, and determining the barium as sulfate.

Catalytic Influence of Cobalt Salts and of Cobalt Salt-Aldehyde Mixtures

In the absence of an oxidation catalyst, the autoxidation of rubber is characterized by a rather prolonged induction period, observed even when the rubber is

* For Part V of this series see P. Schidrowitz, *Bull. Rubber Growers' Assoc.*, 16, 668 (1934).

subjected to careful purification by the standard method of Harries. In the presence of a little cobalt linoleate, however, the induction period is very much reduced, and oxidation proceeds at a greatly enhanced rate. A view has been recently put forward that the function of driers (*e. g.*, cobalt linoleate) in the autoxidation of drying oils is to remove the natural antioxidants present (Stephens, *Ind. Eng. Chem.*, **24**, 918 (1932)), but from the indications obtained in the present work the catalyst would appear to have a very definite accelerating influence on the actual oxidation process in addition to its effect in shortening the initial period of induction (*cf.* Fig. 5, Curves III and VI). Stevens (*Bull. Rubber Growers' Assoc.*, **15**, 600 (1933); B.P. 407,028, 417,912) has shown that among the large number of known rubber viscosity-reducing catalysts the linoleates of the heavy metals are the most effective, and of these the most powerful is cobalt linoleate. It is found by us that though cobalt linoleate is, when acting alone, a much more efficient catalyst than cobalt oleate, yet in the presence of acetaldehyde or paraldehyde the efficiencies of the two salts are of the same order, and indeed the oleate is rather more effective than the linoleate.

A study has also been made of the catalytic influence of other cobalt salts in a benzene solvent in the presence of acetaldehyde at 40° and the following sequence, arranged in order of descending efficiency, worked out: oleate > linoleate > hexoate > hydroxide > butyrate > propionate > acetate or nitrate; the last two salts had practically no catalytic effect during the period under observation. The solvent, however, has a considerable influence on catalyst activity, since cobalt acetate with acetaldehyde was found to be almost as effective as cobalt oleate in a chloroform medium, and for most of the above catalysts a xylene medium was conducive to a higher rate of oxidation than was benzene. It is of interest that suspended cobalt hydroxide is also a fairly good catalyst if used in the presence of acetaldehyde in a chloroform or hydrocarbon solvent, but it was noticed that a little cobalt goes into solution during the oxidation, doubtless owing to the presence of small amounts of acidic substances produced from the rubber or from the aldehyde. As in the case of the linoleates acting alone, cobalt in the form of its salts is again found to be the most effective metal for use together with paraldehyde. The major portion of the paraldehyde added is apparently unchanged during oxidation of the rubber, and indeed only a small quantity need be added in order to achieve the enhanced oxidation activity of the metal catalyst; its action undoubtedly involves intermediate peroxide formation.

Course of Oxidation.—The first stage in the oxidation of a solution of rubber by any of the above catalysts is a reduction of viscosity almost to that of the solvent, accompanied by a change of color (to green in the case of a cobalt salt). Since but little oxygen becomes absorbed and only a trace of carbon dioxide is produced, it is inferred that the reduction in viscosity is not due to any extensive oxidative rupture of the rubber hydrocarbon, but more probably due to an intermolecular breakdown promoted by a trace of oxygen. It is significant that oxidation proceeds to this stage with only a small reduction in the iodine value of the material. Beyond this stage rapid absorption of oxygen begins and proceeds at a fairly uniform rate over a long period; subsequently the rate slackens somewhat, but absorption does not cease altogether even after several days. An analogous behavior has been observed by Kemp, Bishop, and Lasselle (*Ind. Eng. Chem.*, **23**, 1445 (1931)) for pure rubber oxidized in the solid state without a catalyst; in this case oxidation was found not to be complete in 140 days, though reaction had by this time proceeded to an advanced stage.

The absorption of oxygen is accompanied by evolution of carbon dioxide and formation of water, and unless the carbon dioxide in the circulating gas is absorbed

in some part of the apparatus, its accumulation causes the oxidation to slow down and cease prematurely. The rate of oxidation is considerably influenced by temperature; all oxidations have been carried out at as low a temperature as possible (40–50°) compatible with the promotion of a reasonable rate of oxygen absorption, since it is known that at temperatures in excess of 70° even saturated substances may undergo oxidation in the presence of catalysts (*e. g.*, Ellis, *Biochem. J.*, **26**, 791 (1932), reports that stearic acid in the presence of cobalt stearate gives a considerable yield of carbon dioxide at 75°). In those oxidations which have been carried to an advance stage, it has been convenient to raise the temperature to 60° after a time in order to curtail the duration of the experiments.

With a cobalt linoleate catalyst a well-marked stage is reached after the absorption of about half an atom of oxygen per C_5H_8 unit: the color changes from green to brown and a gelatinous material containing much, but not all, of the added cobalt is precipitated. The amount of precipitated material is, however, several times greater than the amount of catalyst added, and must therefore be composed to a large extent of a direct oxidation product. It has the approximate composition $C_{10}H_{16}O_3$ but the analytical figures obtained for this product must be regarded as approximate only, since it could not be completely freed from cobalt salts. It is to be noted that Herbst (*Ber.*, **39**, 523 (1906)) subjected a solution of purified rubber to the action of oxygen for 140 hours at 80°, and obtained a soluble resin of the composition $C_{10}H_{16}O$ and an insoluble friable precipitate of the composition $C_{10}H_{16}O_3$. The formation of insoluble matter in the present work appears to be dependent on the presence of the catalyst, for it is observed that if after precipitation of the insoluble matter the liquor is filtered and the filtrate subjected to further oxidation, no additional insoluble matter is produced, but if more catalyst is added and the filtrate then further oxidized, insoluble matter is again precipitated after a few hours. Moreover with a cobalt catalyst, operating in the presence of aldehyde, the amount of insoluble matter precipitated is much less and is in this case comparable with the quantity of catalyst added. The insoluble precipitated material cannot itself be further oxidized.

The upper limit of oxidation reached in the present work is that represented by the introduction of three oxygen atoms into the double unit, $C_{10}H_{16}$, and at this stage about one in every 30 carbon atoms of the rubber skeleton has suffered oxidation to carbon dioxide, while for each carbon atom so oxidized approximately six hydrogen atoms have been oxidized to water. At the earlier stage of oxidation represented by the absorption of one atom of oxygen per $C_{10}H_{16}$ unit, one in approximately every 300 carbon atoms of the rubber skeleton has undergone oxidation to carbon dioxide.

Comparative Rates of Oxidation

The first set of curves (Fig. 1) shows the relative efficiencies of various metal catalysts in promoting oxidation in the presence of paraldehyde. It is apparent that cobalt is the only metal with ability to promote any very greatly enhanced rate of oxidation; other metals promote only very limited absorption of oxygen and bring about only slight reduction of viscosity in a period of two hours. With cobalt the viscosity is reduced to a minimum within five or ten minutes, and rapid oxygen absorption sets in from the start. Cobalt oleate acting alone does not promote any change in either viscosity or susceptibility towards oxidation during a period of 8 hours, nor does paraldehyde acting alone produce any change. In Fig. 2 the rate of absorption of cobalt oleate is compared with that of cobalt linoleate, both substances being employed in the presence of paraldehyde; the curves show that oxidation proceeds rather more rapidly with the oleate than with the

linoleate catalyst, but the catalytic influence of the aldehyde is clearly to be seen by comparing the oxidation curves for these salts when acting with aldehyde with those for the same salts acting alone, as shown in Figs. 1 and 2.

The apparent increase in oxidation velocity arising from the substitution of acetaldehyde for paraldehyde is shown in the curves in Fig. 3, but since the cobalt

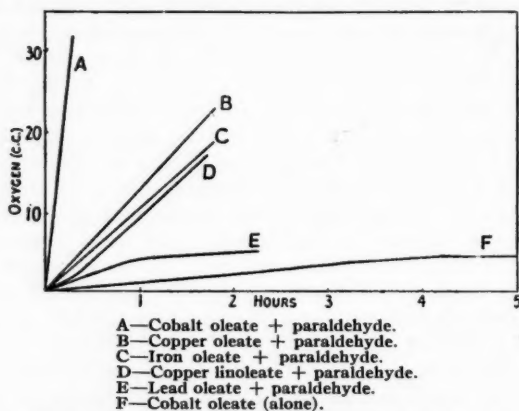


Figure 1—Rates of Oxidation Observed with 5 G. of Milled Rubber in 50 Cc. of Xylene, 0.3 G. of Catalyst, and 2 Cc. of Paraldehyde

oleate acetaldehyde catalyst is of itself able over the range depicted to absorb more oxygen than is absorbed by the rubber (see Fig. 4), the observations made with this catalyst have been disregarded. The period of rest observed soon after the beginning of absorption with cobalt oleate-acetaldehyde in the presence of

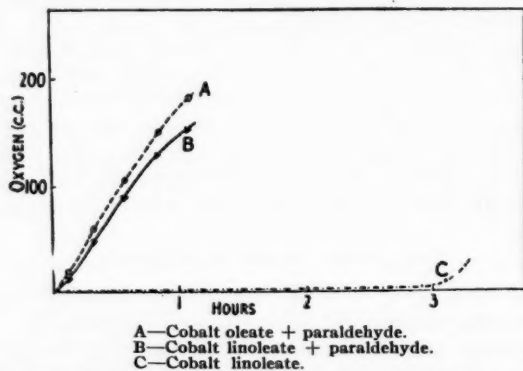


Figure 2—Rates of Oxidation Observed with 5 G. of Milled Rubber in 50 G. of Xylene, 0.3 G. of Catalyst, and 2 Cc. of Paraldehyde (Where Used)

rubber indicates that the direct oxidation of the acetaldehyde is arrested for a time by the rubber. It will be observed that the curve for cobalt oleate and paraldehyde in Fig. 3 does not duplicate the curve for the same catalyst in Fig. 2. This is not due to experimental variation, but to the fact that a fresh sample of rubber was used in obtaining the data for both curves in Fig. 3; this new sample showed

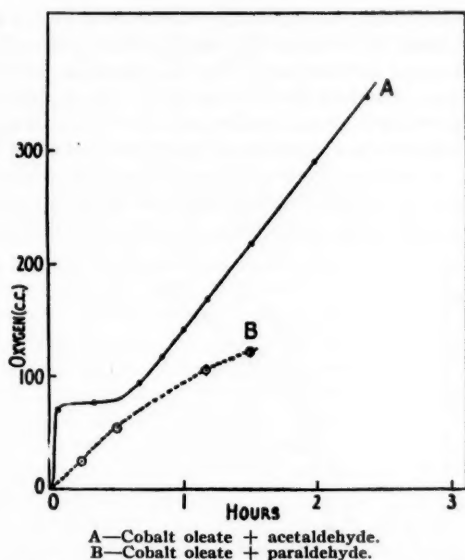


Figure 3—Rates of Oxidation of 5 G. of Milled Rubber in 50 G. of Xylene, with 0.3 G. of Cobalt Oleate and 2 Cc. of Paraldehyde or Acetaldehyde

an induction period of 6 hours with a cobalt linoleate catalyst in the absence of aldehyde.

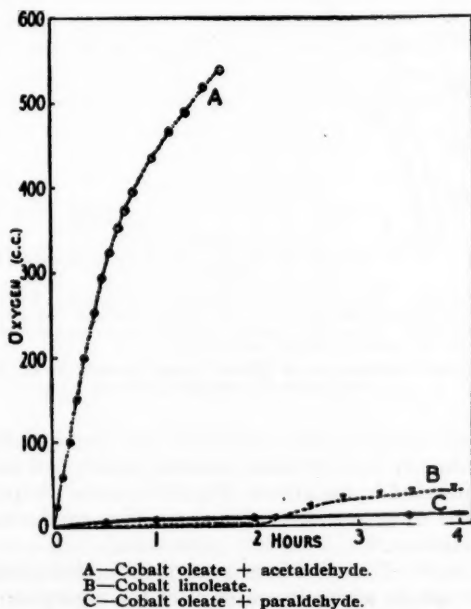
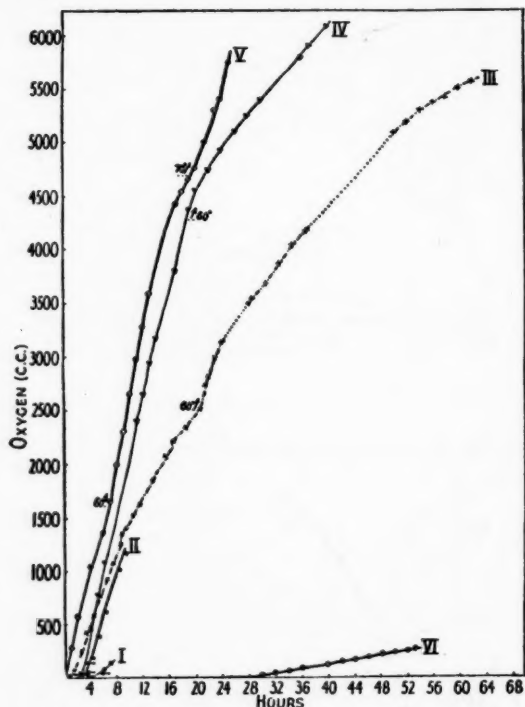


Figure 4—Oxygen Absorption of Various Catalysts (0.3 G. of Cobalt Salt and, Where Employed, 2 Cc. of Paraldehyde or Acetaldehyde in 50 Cc. of Xylene)

No attempt has been made to purify the rubber used in our experiments, since it was especially desired to observe the comparative rates of oxidation for the natural product. Except in the case of the cobalt oleate-acetaldehyde catalyst, the amount of oxygen absorbed by the catalysts was negligible compared with that absorbed by the rubber, as can be seen by reference to Fig. 4. The progress of reaction when oxidation is carried to an advanced stage is shown for various catalysts in Fig. 5; it will be observed that the rate of oxidation is slower in a benzene medium than in xylene. A very efficient catalyst combination has been found in cobalt linoleate-acetic anhydride, the strong activity of which became



Solvent: xylene (Curve I, benzene). Catalysts: Curves I-III, cobalt linoleate; Curve IV, cobalt linoleate and acetic anhydride; Curve V, cobalt linoleate and paraldehyde; Curve VI (purified rubber), no catalyst.

Figure 5—Oxidation of Milled Crepe Rubber (15 G.) in Presence of Various Catalysts

apparent when acetic anhydride was introduced into the oxidation mixtures in an attempt to acetylate any hydroxylated material which had been formed. The horizontal arrows inserted in the curves (Fig. 5) indicate the points at which the viscosity was reduced to a minimum. Discontinuities are due to overnight interruptions of the oxidations.

Removal of the Cobalt.—Though a large part of the added cobalt is carried down in an insoluble precipitate which separates after the absorption of about half an atom of oxygen per C_5H_8 unit, the residual solution still contains traces of the metal. The catalyst can, however, be quantitatively removed at any stage of the oxidation

by precipitation with the theoretical quantity of a solution of thioglycollic acid followed by filtration (cf. Long, Zimmermann, and Nevins, *Ind. Eng. Chem.*, **20**, 809 (1928)), and if to the clear, almost colorless solution so obtained a trace of an antioxidant is added, the solution will not undergo further oxidation for a considerable period of time. By this means the oxidized rubber can be obtained in a form suitable for incorporation into ordinary rubber or latex for various technical purposes.

Other Oxidation Catalysts

Solutions of rubber in tetralin have been observed to suffer a reduction of viscosity on keeping (Staudinger, *Annalen*, **488**, 127 (1931)), and it is known that tetralin forms a stable peroxide on exposure to air (Hock, *Ber.*, **66**, [B], 61 (1933)). No advantage, however, was found to accrue by the use of tetralin as a solvent in the present work. Some oxidation occurs on shaking a rubber solution with aqueous potassium ferrieyanide and sodium carbonate, but the amount of these salts required is too great to make this method worthy of further consideration (cf. Wright, Conant, and Kamerling, *J. Biol. Chem.*, **94**, 411 (1931)). A number of acids are known to effect a reduction of viscosity of rubber solutions (Shimada, *J. Soc. Chem. Ind. Japan*, **37**, 309B (1934)), and in the present work it is found that the reduction of viscosity occurring when acetic acid is added to a rubber solution is actually caused by oxidation, carbon dioxide being found in the atmosphere above the surface of the solution, and an appreciable oxygen content being revealed on analysis of the modified rubber so produced.

Products of Oxidation

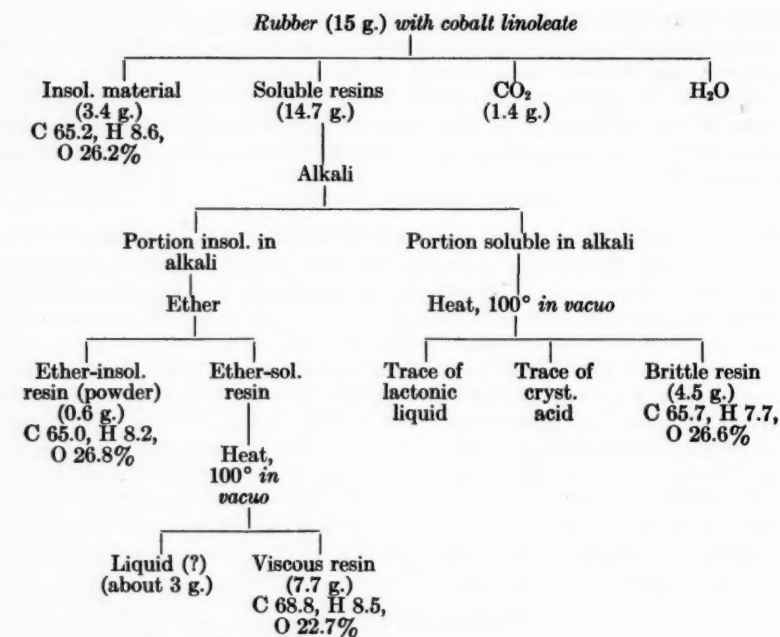
The product of an oxidation process interrupted at the stage at which viscosity is reduced to a minimum, *i. e.*, prior to the absorption of any considerable quantity of oxygen, is a plastic, rather tacky mass possessing some rubber-like properties, and in fact closely resembling a very much softened rubber; it is soluble in the usual solvents for rubber and in ether. As oxidation proceeds further the product becomes more tacky and more fluid, until at the stage represented by the introduction of half an atom of oxygen per C_5H_8 unit it is a gum which is soluble in rubber solvents, ether, and also in ethyl acetate; on further oxidation the product becomes more resinous and becomes amenable to a separative treatment by distillation and solvent extraction, the formation of volatile ketonic products affording definite indication of severe disruption of the rubber molecule. The most highly oxidized materials isolated are brittle resins, soluble in alcohol, acetone, and aqueous alkali, and represent the oxidation stage at which three atoms of oxygen have entered the double unit $C_{10}H_{16}$. The nature, composition, and properties of the products isolated in typical operations are set out in the following tables.

Oxidation in Presence of Cobalt Linoleate (0.6 G.).—15 g. of rubber absorbed 5637 cc. of O_2 and yielded 1.4 g. of CO_2 , *i. e.*, 1 carbon atom in $7C_5H_8$ units become oxidized to CO_2 . The oxygen absorption calculated on the basis of the isolated products = 5300 cc.

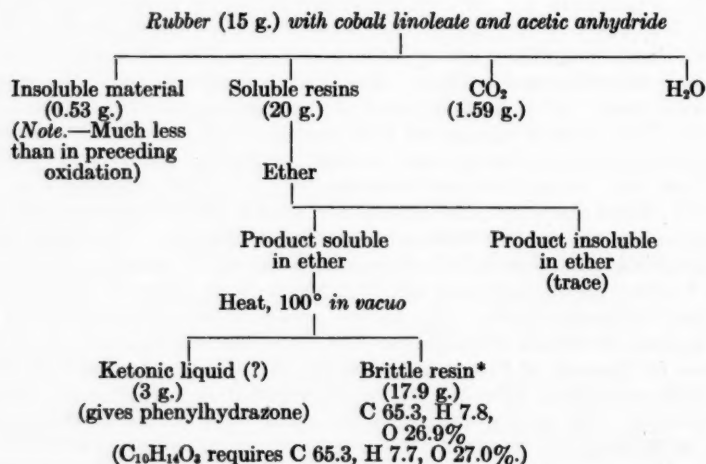
Oxidation in Presence of Cobalt Linoleate and Acetic Anhydride.—15 g. of rubber absorbed 6135 cc. of O_2 and yielded 1.59 g. of CO_2 . The oxygen absorption calculated on the basis of the products isolated was 5840 cc.

Oxidation in Presence of Cobalt Oleate (0.6 G.) and Paraldehyde (10 Cc.).—15 g. of rubber absorbed 5765 cc. of O_2 and yielded 1.61 g. of CO_2 .

The course of catalyzed oxidation appears to follow closely the observations of Kemp, Bishop, and Lasselle (*loc. cit.*), the products being unsaturated acidic substances containing much peroxidic oxygen, but apparently no hydroxylic groupings,

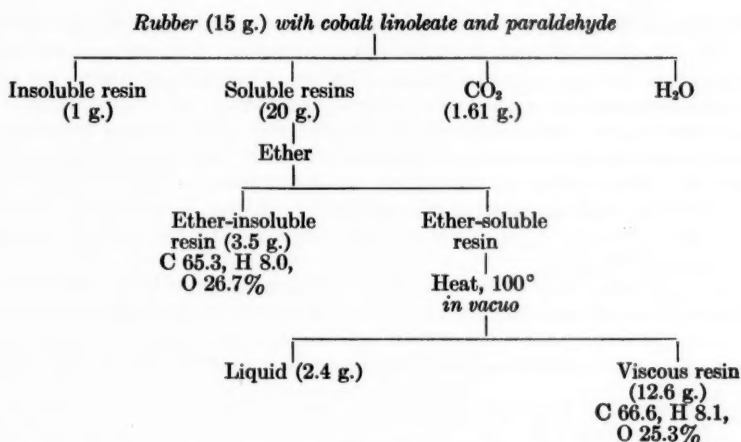


NOTE.— $C_{10}H_{16}O_2$ requires C 65.2, H 8.7, O 26.1%.



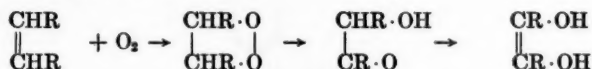
since it has not been found possible to acetylate the resins to any appreciable extent. Catalytic hydrogenation in the presence of a platinum, palladium, or nickel catalyst at atmospheric temperature and pressure reduces the peroxidic linkings (presumably to hydroxyl groups) but leaves the resins still markedly unsaturated toward permanganate and toward bromine. That peroxide groups are formed at unsaturated centers in the autoxidation of vegetable drying oils is already well

* This resin could not be saponified, so did not appear to be acetylated.



established by the work of Morrell and Marks (*J. Oil Col. Chem. Assoc.*, 12, 183 (1929)), but in the case of these oils the process of oxidation is complicated by polymerization (*i. e.*, gelation), a phenomenon which is not apparent in the present work. Some indications have, however, been obtained (Long and McCarter, *Ind. Eng. Chem.*, 23, 786(1931)) that cobalt driers favor an oxidative type of reaction, while lead and certain other metal driers favor gelation.

Up to quite an advanced stage of oxidation the products have many of the chemical properties of rubber itself, *i. e.*, they can be chlorinated, hydrochlorinated, hypochlorinated, polymerized by the action of sulfuric acid or metallic chlorides, and can form nitroso-derivatives with oxides of nitrogen. The existence of marked double-linking unsaturation in the oxidation products cannot, however, be immediately assumed, since Long and McCarter (*loc. cit.*) have postulated that the peroxidic groupings can, in virtue of a tautomeric rearrangement, behave as hydroxylated unsaturated centers, thus:



A comprehensive study of the properties and chemical nature of the oxidation products is at present in hand, and it is hoped later to publish the results of this work.

The products which are isolated in the early stages of oxidation undergo slow drying in the air, especially when treated with a little cobalt linoleate and exposed in thin films. This phenomenon is, however, not simply one of further oxidation, since the dried resins are insoluble in all solvents, whereas by further oxidation in solution soluble resins are obtained. It has also been observed that the resin $\text{C}_{10}\text{H}_{16}\text{O}$ when preserved free from solvent becomes (even in an atmosphere of nitrogen) appreciably less soluble in the course of a week, and it seems probable that the drying is to be accounted for by a process of polymerization or gelation; this matter also is under further investigation.

Experimental

Experiments with Acetaldehyde.—Dry oxygen was passed through acetaldehyde containing 0.5% by weight of cobalt acetate at -20° . After a few hours crystals

of peracetic acid separated, but the preparation was ended by a violent explosion before all of the acetaldehyde had undergone oxidation. Oxygen was next passed into a solution of 10 g. of milled crepe in 200 cc. of chloroform containing 10 cc. of acetaldehyde and 0.5 g. of cobalt acetate; no change was apparent at -20° during several hours, but on warming to 40° the pink color changed to green, and in a very short time the viscosity of the solution was reduced practically to that of the solvent. Evaporation of the solvent yielded a resinous mass (found C 82.9 H 11.1, O 6.0%), soluble in ether and in rubber solvents, which slowly hardened on exposure to the air; its drying was greatly expedited by the addition of a little cobalt linoleate drier.

Influence of Cobalt Salts.—To 60 cc. of a benzene solution of 10 g. of milled crepe were added 4 cc. of acetaldehyde and 0.2 g. of one of the following cobalt salts: (1) acetate, (2) propionate, (3) butyrate, (4) hexoate, (5) oleate, (6) linoleate, (7) nitrate (anhydrous), (8) hydroxide. Oxygen was passed simultaneously through

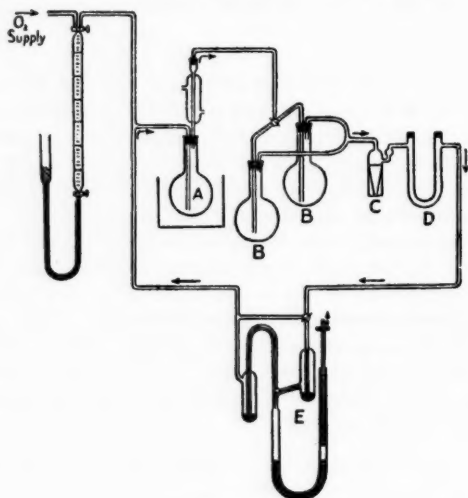


Figure 6

each solution at 40° ; the viscosity of solutions (5) and (6) was reduced to that of the solvent in $\frac{3}{4}$ hour, and the corresponding change in the other solutions followed in the sequence $5 > 6 > 4 > 8 > 3 > 2 > 1$. No change was apparent in (1) or in (7) during 8 hours. The product isolated in each case appeared to be of the same nature as that isolated from the above oxidation carried out in chloroform solution. With a cobalt oleate catalyst an amount of catalyst equal to 2–3% of the weight of rubber used was sufficient, and the proportion of acetaldehyde used could be reduced to 20% of the weight of rubber present without seriously affecting the rate of viscosity reduction. The cobalt oleate catalyst was found to be even more effective when the acetaldehyde was replaced by paraldehyde; the rate of viscosity reduction was then much increased, and in fact became practically complete within a few minutes of adding the paraldehyde. Indeed, so active was the combination of these two substances that it was found possible to prepare a rubber solution of high concentration and low viscosity simply by shaking crumb rubber (25 g.) with benzene (100 cc.) containing paraldehyde (10 cc.) and cobalt oleate (0.75 g.) in the air at 40° . It was further found possible to reduce the amount of

paraldehyde used as a viscosity reducer. In the presence of cobalt oleate alone, or of paraldehyde alone, no reduction of viscosity occurred in 8 hours.

For convenience at this stage, stock benzene solutions of cobalt oleate and linoleate were prepared. The oleate was precipitated by mixing aqueous solutions of cobalt nitrate and sodium oleate, and the linoleate was similarly precipitated from an aqueous-alcoholic solution of ammonium linoleate; both salts were dried *in vacuo* at 100° and dissolved in sufficient benzene to give a 10% solution. It was found that unless about 1% of alcohol was also present in the solutions, gelation occurred in a short time.

It was noticed that a little carbon dioxide was produced on continuing the passage of oxygen into the rubber solutions after reduction of viscosity, and a circulating apparatus was designed in order to study the oxidation process quantitatively; the nature of this apparatus is indicated in Fig. 6.

Apparatus for Oxidation.—Flask A contains the solution undergoing oxidation, and the twin flasks B and B contain baryta water to absorb carbon dioxide, either flask being placed in circuit at will by a turn of the three-way tap. Before passing to the circulating pump (E), the oxygen employed is dried by sulfuric acid in C and calcium chloride in D; the sulfuric acid is somewhat diluted in order to avoid sulfonation of solvent vapors. Oxygen is supplied to the apparatus after purification by passage through aqueous permanganate, caustic potash, and sulphuric acid consecutively, the oxygen intake being measured by the contraction occurring in the gas burette.

Catalyst Efficiency.—In each of the following experiments 5.0 g. of milled crepe, dissolved in 100 cc. of xylene, were treated with 0.3 g. of metal oleate or linoleate and 2.0 cc. of aldehyde at 50°.

	Time After Start, Min.	Oxygen Absorbed, Cc.
(i) Cobalt oleate with no added aldehyde	240	5.1 (a)
	480	None
(ii) Cobalt linoleate with no added aldehyde	165	0.3
	180	1.8 (b)
	190	11.4 (c)
	200	16.4 (d)
(iii) Cobalt oleate with paraldehyde	5	7.0 (e)
	10	16.7
	20	57.0
	35	106.8
	50	147.9
	65	185.8
(iv) Cobalt linoleate with paraldehyde	10	10.8 (f)
	20	45.8
	35	89.9
	50	128.1
	65	156.2
(v) Cobalt oleate with paraldehyde (different batch of milled crepe)	15	25.0 (g)
	30	55.8
	70	107.4
	90	127.4
(vi) Cobalt oleate with acetaldehyde [rubber from the same batch as in (v)]	3	70.6 (k)
	20	73.0 (l)
	40	93.4 (m)
	50	116.0
	60	141.2
	70	165.6
	90	218.6

100	242.2
110	266.7
120	291.2
130	315.2
140	339.5
150	364.0

Observations.—(a) No change in viscosity or color. (b) Viscosity lower. (c) Color green. (d) Viscosity reduced to minimum. (e) Viscosity much reduced; color green. (f) Viscosity much reduced; color green. (g) Viscosity reduced. No change occurred in 6 hours in presence of cobalt linoleate alone. (k) Viscosity slightly reduced; color brown. (l) No great change. (m) Viscosity reduced; color green.

The following oxidations were carried out with the same rubber as was used in experiments (i) to (iv):

	Time After Start, Min.	Oxygen Absorbed, Cc.
(vii) Copper linoleate with paraldehyde	50	6.6
	70	12.6
	85	15.0
	100	16.6 (n)
(viii) Copper oleate with paraldehyde	20	4.6
	60	13.2
	90	18.3
	100	21.2 (h)
(ix) Ferric oleate with paraldehyde	25	0.8
	45	8.7
	75	15.2
	105	16.6 (i)
(x) Lead oleate with paraldehyde	45	4.0
	85	4.6
	130	5.2 (j)

Observations.—(n) Viscosity slightly reduced. (h) Viscosity slightly reduced. (i) Viscosity only slightly reduced. (j) Viscosity unchanged.

It was also observed that the oleates of nickel, chromium, manganese, and zinc, acting with paraldehyde, had very little effect on viscosity during periods comparable with those employed above.

In the following experiments the same weight of catalyst, aldehyde, and xylene were taken, but no rubber was present.

	Time After Start, Min.	Oxygen Absorbed, Cc.
(xi) Cobalt oleate with paraldehyde	30	5.2 (o)
	60	9.0
	120	11.0
	210	14.4 (p)
(xii) Cobalt oleate with acetaldehyde	3	25.8 (q)
	7	60.2
	10	101.0
	15	149.7
	20	204.0 (r)
	25	255.2
	30	291.5
	35	328.2
	40	355.5
	50	396.5
	60	436.3
	70	466.7
	80	492.3
	90	521.1
	100	540.7 (s)

(xiii) Cobalt linoleate with no added aldehyde	120	2.0
	140	10.0
	153	22.0
	172	31.0
	192	36.5
	212	43.2
	237	45.0 (u)

Observations.—(o) Color green. (p) No material precipitated during oxidation. (q) Color green. (r) Some material precipitated. (s) In this oxidation most of the cobalt was precipitated and the solution was found to contain acetic acid and much peroxidic material. (u) All of the cobalt became precipitated as a gelatinous mass and no further oxygen absorption occurred; 0.0134 g. of carbon dioxide was formed.

Inhibition of Oxidation.—Oxidation of rubber in the presence of cobalt catalysts, with or without added aldehyde, was inhibited for a long period by a trace of quinol or by a drop of sulfuric acid.

Other Oxidation Catalysts

(1) *Tetralin.*—A current of air was drawn through 50 g. of tetralin for 60 hours at 70°. The unchanged tetralin was then removed under a vacuum of 0.1 mm., leaving tetralin peroxide (7 g.) as a viscous resin which was dissolved in benzene and added to a solution of 10 g. of milled crepe in 100 cc. of benzene. The product maintained at 50° showed only a small change in viscosity after several days. When air or oxygen was drawn through a solution of rubber in tetralin, the viscosity became somewhat reduced after 24 hours; in the presence of cobalt linoleate oxidation did not proceed any more rapidly in tetralin than in benzene.

(2) *Potassium Ferricyanide.*—Twenty cc. of a 2.5% rubber solution in benzene were shaken with 100 cc. of an aqueous solution of 4.1 g. of potassium ferricyanide and 0.5 g. of anhydrous sodium carbonate in oxygen at room temperature and pressure; in 40 hours only 12 cc. of oxygen had become absorbed.

(3) *Acetic Acid.*—The addition of acetic acid to a solution of rubber containing cobalt linoleate greatly enhanced the rate of oxidation and yielded after 24 hours a resin soluble in most solvents except alcohol and partly soluble in alcoholic caustic soda. The addition of acetic acid alone to a rubber solution brought about a reduction of viscosity which became apparent after a few days at room temperature; e. g., 4 cc. of the acid added to 20 cc. of a 12.5% solution of milled crepe in benzene reduced the viscosity to that of the solvent in the course of 10 days. A trace of sulfuric acid did not inhibit this reaction, for although it had been anticipated that the addition of acetic acid containing 0.33% by weight of sulfuric acid would promote polymerization (cf. Wagner-Jauregg, *Annalen*, **496**, 52 (1932)), actually oxidative degradation occurred. Thus when to 100 cc. of a 12.5% solution of milled crepe in benzene were added 42 cc. of 0.33% sulfuric acid in acetic acid, and the mixture was first agitated until homogeneous and then left for 3 weeks at room temperature, it was found that the viscosity had become reduced to that of the solvent, and some carbon dioxide was present in the atmosphere above the solution. The reaction product in this example, when isolated by precipitation, was obtained as a resinous mass containing oxygen (found C 84.3, H 11.2, O 4.5%).

Oxidations Carried to an Advanced Stage in the Presence of Catalysts.—In each of the experiments described in the following sections, acetone-extracted milled crepe (15 g.) was dissolved in a solvent (200 cc.) and oxidized at 50° in the presence of the stated catalysts. Except in the first experiment, in which the solvent was benzene, xylene which had been purified by shaking once with concentrated sulfuric acid was employed.

I. *Catalyst: 0.6 G. of Cobalt Linoleate.*—Reduction in viscosity occurred after an induction period of 4 hours, and oxidation proceeded with evolution of carbon dioxide; 145 cc. of oxygen were absorbed over a period of $2\frac{3}{4}$ hours, after which the oxidation was stopped. The course of this oxidation is shown in Fig. 5, Curve I.

II. *Catalyst: 0.6 G. of Cobalt Linoleate.*—Reduction in viscosity occurred after an induction period of $2\frac{1}{4}$ hours, and absorption of oxygen commenced with simultaneous evolution of carbon dioxide. After an absorption of 1183 cc. (n.t.p.) of oxygen the oxidation was stopped, and the apparatus evacuated and filled with nitrogen; no further amount of carbon dioxide was formed, indicating that this gas arises from direct oxidation of the rubber, and not by slow decomposition of peroxide material. The barium carbonate precipitated was filtered off and yielded 0.883 g. of barium sulfate (= 0.167 g. CO_2). The course of oxidation is shown in Fig. 5, Curve II. The oxidation product, isolated by filtration and evaporation (*in vacuo*) of the xylene solution, was a resinous mass with slight elastic properties. It was soluble in rubber solvents and in ether and ethyl acetate, but only partly soluble in alcohol and acetone. It had the empirical composition $\text{C}_{10}\text{H}_{15.8}\text{O}_{6.96}$ (found C 79.4, H 10.45%).

The resin showed marked peroxidic properties, liberating iodine from potassium iodide and producing a pronounced red coloration with a solution of ammonium thiocyanate and ferrous ammonium sulfate. It could not be distilled since it decomposed at about $240\text{--}250^\circ$ under a few mm. pressure, giving volatile material of rather pleasant odor. Towards bromine and permanganate it showed pronounced unsaturation; its iodine value was 343. On attempting to hydrogenate the resin catalytically at atmospheric temperature and pressure in ethyl acetate solution in presence of platinum, palladized calcium carbonate, or Raney's nickel catalyst, a very little hydrogen was absorbed and the product, although now freed from peroxidic oxygen, was still unsaturated. The resin was very feebly acidic towards alkalis; 0.4 g. of resin (dissolved in benzene) required 3.5 cc. of 0.05 *N*-baryta, the end-point of titration being very indefinite. Extraction of the resin with alcohol before titration removed only a trace of material but reduced the titer value to 0.5 cc. of 0.05 *N*-baryta per 0.4 g. of resin. Some heat was evolved on treating the resin with thionyl chloride in benzene solution, but no hydrogen chloride was liberated.

In an attempt to acetylate any hydroxylic component of the resin which might be present, 2-g. portions were dissolved in xylene and refluxed with acetic anhydride in the presence of (a) sulfuric acid, (b) potassium acetate, and (c) acetyl chloride. All traces of acetic acid were then removed by successive partial distillation and washing with alcohol. The resin was in each case finally dissolved in benzene and boiled with alcoholic caustic potash, but in no single case could any potassium acetate be isolated from the alkaline solution.

Acetic anhydride (10 cc.) was next added to a rubber solution containing 6 g. of rubber and 0.2 g. of cobalt linoleate, and oxygen was bubbled through the solution. Reduction of viscosity was very rapid, and the oxidation product isolated after 24 hours was a resin which was soluble in acetone, alcohol, acetic acid, and ether, as well as in rubber solvents, and was also partly soluble in aqueous alkali, indicating that oxidation had proceeded to a much more advanced stage than had been experienced in the foregoing experiments. The acetone solution of the resin was markedly unsaturated towards permanganate. After removal of all traces of acetic acid and anhydride by repeatedly pouring the alcoholic solution of the resin into water, the resin was dissolved in alcoholic caustic potash and refluxed for 4 hours. The solution so obtained was then successively diluted with water, acidified, filtered free from precipitated resin, neutralized with ammonia,

and concentrated; the residual salts gave definite indications of the presence of acetate, and ultimately acetic acid was isolated and positively identified in the form of its *p*-bromophenacyl ester, m. p. 85°.

III. *Catalyst: Cobalt Linoleate (0.6 G.)*.—This oxidation was allowed to proceed until the rate of oxygen absorption showed definite indications of slowing down. After 1500 cc. of oxygen had been absorbed, a considerable amount of gelatinous material was precipitated; after 5637 cc. had been absorbed (during a period of 60 hours) the oxidation was stopped. In order to reduce the time required for this absorption, the temperature was raised to 60° at a point when 2750 cc. of gas had been taken up. The course of oxidation is shown in Fig. 5, Curve III.

A tenth part of the barium carbonate formed yielded, on conversion into sulfate, 0.7410 g. of barium sulfate, whence the total carbon dioxide produced was 1.4 g.—an amount equivalent to the oxidation of one in every 35 carbon atoms of the carbon skeleton.

The oxidized solution was filtered free from the precipitated insoluble matter, which, after being washed, dried to a pale brown powder (3.4 g.) containing cobalt salts (borax bead test). This powder was insoluble in all solvents but gave on treatment with aqueous alkali a turbid solution from which no material was precipitated on acidification. The powder (2 g.), suspended in xylene absorbed no oxygen when replaced in the oxidation apparatus at 50°. For analysis it was purified as far as possible by suspending it in alcohol containing a little hydrochloric acid and subsequently washing it and extracting it with solvents. It gave C 65.2, H 8.6%, allowance being made for the cobalt salt contained therein, the latter being calculated on the ash content. These figures correspond to the composition $C_{10}H_{15.8}O_3$. Evaporation of the filtrate yielded a viscous resin (14.7 g.) soluble in acetone, almost wholly soluble in alcohol, partly soluble in ether and in aqueous alkali. That this resin contained a little cobalt was shown by a borax bead test. The following separative procedure was then adopted. The resin was dissolved in acetone and poured into aqueous alkali; the alkaline liquor so obtained was first extracted with benzene, then acidified, and extracted with ether.

The ether extract yielded a nearly solid resin which on heating at 100°/0.1 mm. yielded a trace of volatile lactic acid and a trace of a crystalline solid; the residue was a brittle resin (4.5 g.) (found C 65.7, H 7.7%, equivalent, by titration, 346, corresponding to the empirical composition $C_{10}H_{14.1}O_3$).

The benzene extract yielded a resin which was partly soluble in ether; the insoluble portion gave on drying a pale yellow powder (0.6 g.) (found C 65.0, H 8.2%, equivalent 1550, corresponding to the empirical composition $C_{10}H_{15.2}O_{3.1}$). The ether-soluble portion yielded on heating at 100°/0.1 mm. about 2 g. of liquid and a viscous residue (found C 68.8, H 8.5%, equivalent 6100, corresponding to the empirical composition $C_{10}H_{14.8}O_{2.6}$).

Influence of Catalyst on Precipitation of Insoluble Matter.—A 15-g. portion of milled crepe was subjected to oxidation under the conditions described in Section III, but oxidation was stopped when 1500 cc. of oxygen had been absorbed. The solution was freed by filtration from precipitated insoluble matter and divided into two parts. To the first part 0.3 g. of cobalt linoleate was added, and the solution again subjected to oxidation; this oxidation proceeded initially at a rate of 200 cc. per hour, more insoluble matter being precipitated after five or six hours, by which time the rate of oxygen absorption had decreased to 100 cc. per hour. The second half of the solution was submitted to further oxidation without the addition of more catalyst; absorption of oxygen continued steadily at a rate of 50 cc. per hour over a period of 20 hours, during which time no insoluble matter was precipitated.

IV. *Oxidation in the Presence of Acetic Anhydride. Catalyst: 0.6 G. of Cobalt Linoleate and 25 Cc. of Acetic Anhydride.*—Viscosity reduction and oxygen absorption commenced after an induction period of $2\frac{1}{2}$ hours, the rate of the latter (Curve IV) being considerably greater than with cobalt linoleate acting alone. In all 6135 cc. of oxygen were absorbed during 30 hours, 1.59 g. of carbon dioxide being produced; in this oxidation, however, only 0.53 g. of insoluble matter was precipitated. The filtered product was first treated with 20 cc. of methyl alcohol in order to esterify the unchanged acetic anhydride and then evaporated. A brown viscous resin (20 g.) was obtained, which was soluble in alcohol, acetone, ether, acetic acid, hydrocarbons, and chlorinated hydrocarbons. The acetyl value of the resin was found in the following way. An alcoholic solution of 0.51 g. was neutralized with 0.37 *N*-alcoholic potash (2.04 cc. required to give a reasonably permanent end-point at 0°), and then refluxed for 6 hours with a further 25 cc. of the potash solution; simultaneously 25 cc. of the potash solution were diluted with alcohol until equal in bulk to the foregoing alkaline liquor and boiled for 6 hours. The two solutions required for neutralization 14.8 cc. and 15.5 cc. of 0.502 *N*-sulfuric acid, respectively, indicating that the percentage of acetylated hydroxyl groups present in the resin was very small (4% calculated as % OAc). The remainder of the resin (19.4 g.) was heated at $100^\circ/0.01$ mm.; it yielded 2 g. of a fragrant liquid, leaving a residual brittle resin (17.9 g.) which was almost wholly soluble in ether (found C 65.3, H 7.8%, equivalent 670, corresponding to the empirical composition $C_{10}H_{14.3}O_{3.1}$). The redistilled liquid (b. p. $65-110^\circ/11$ mm.) was insoluble in water and in alkali, was unsaturated towards permanganate, gave positive peroxidic reactions with potassium iodide and with aqueous ammonium thiocyanate-ferrous sulfate solution, and yielded a phenylhydrazone (m. p. $68-70^\circ$) which suffered rapid oxidation in the air. On catalytic hydrogenation with Raney's nickel catalyst at room temperature and pressure, the volatile liquid (0.68 g.) absorbed hydrogen (75 cc.) to yield a peroxide-free liquid which was stable to permanganate and yielded no phenylhydrazone.

V. *Acceleration of the Rate of Oxidation by Use of Paraldehyde. Catalyst: 0.6 G. of Cobalt Oleate and 10 Cc. of Paraldehyde.*—Reduction of viscosity commenced within three minutes of adding the catalyst, and absorption of oxygen together with formation of carbon dioxide commenced 10 minutes later (see curve V). Some insoluble matter (1.0 g.) separated after 2500 cc. of oxygen had been absorbed, and the oxidation was discontinued after 5765 cc. of oxygen had been absorbed. The time taken was 26 hours, during which 1.61 g. of carbon dioxide was produced. The filtered oxidation product yielded on evaporation 19.6 g. of resin, which on extraction with ether left a brittle ether-insoluble resin (3.5 g.) soluble in acetone, alcohol, hydrocarbons, and chlorinated hydrocarbons (found C 65.3, H 8.0%, corresponding to the empirical composition $C_{10}H_{14.7}O_{2.1}$). The ether extract yielded on heating at $100^\circ/0.01$ mm. 2.4 g. of a volatile liquid similar to that described in Section IV above, and 12.6 g. of a viscous resin (found C 66.6, H 8.1%, corresponding to the empirical composition $C_{10}H_{14.6}O_{2.9}$).

VI. *Comparative Oxidation of Purified Milled Crepe Rubber in the Absence of a Catalyst.*—This oxidation was carried out with milled crepe rubber which had been carefully purified by precipitation and by acetone extraction. A solution of the purified rubber (15 g.) in pure xylene (150 g.) underwent slow reduction of viscosity after an initial induction period of 27 hours; complete reduction, however, did not occur until 4 hours later, at which point 24 cc. of oxygen had been absorbed, and traces of carbon dioxide had become apparent. The course of oxidation is shown in Fig. 5, Curve VI.

Removal of Catalyst from Cobalt-Catalyzed Oxidations.—On adding a slight excess

of a benzene solution of thioglycollic acid to a solution of 15 g. of oxidized rubber (the latter containing 1 atom of oxygen per $C_{16}H_{16}$ unit) and leaving the product overnight, a gelatinous precipitate containing all the cobalt separated. The filtered solution when replaced in the oxidation apparatus took up oxygen only very slowly (5 cc. oxygen per hour), and even this slow absorption was found to be totally inhibited for 20 hours when a trace of quinol was added; after this period oxidation recommenced at the rate of 3 cc. per hour.

Atmospheric Drying of the Resins.—The resinous products obtained up to an advanced stage of oxidation dried slowly in the air, yielding tough masses which were insoluble in all solvents except alcoholic alkali. A thin film of a resin $C_{16}H_{16}O$ was prepared on a glass plate by evaporation of a benzene solution of this product; this film after three weeks' exposure to air had attained constant weight and when peeled off and powdered gave C 69.5, H 8.9%.

Further studies of the chemical properties of the above-described products, and of the changes in chemical properties which accompany the progressive oxidation of rubber, are at present in hand.

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The Oxidation of Rubber by Hydrogen Peroxide

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It was noticed long ago that rubber changes during storage, and that it loses its valuable qualities. Many authors have tried to explain this phenomenon as a union of oxygen with rubber molecules.

The most interesting work on this subject was the early work of Herbst (*Ber.*, **39**, 523 (1906)). Herbst blew air for 140 hours through benzene solutions of rubber and obtained two products, $C_{10}H_{16}O_3$, as a main product, and $C_{10}H_{16}O$, as a very small admixture.

Later Peachey and Leon (*J. Soc. Chem. Ind.*, **31**, 1103 (1912); **37**, 55 (1918)) subjected rubber films to the action of oxygen and found that for each group of $C_{10}H_{16}$, four atoms of oxygen were added and one atom of carbon was liberated. These workers succeeded in separating several compounds with different degrees of oxidation, viz., $C_{10}H_{16}O$; $C_{10}H_{16}O_4$; $C_6H_8O_2$.

Herbst thought that he had obtained an addition product of oxygen and rubber hydrocarbon, but Peachey considered that the compounds were the result of a splitting and depolymerization of the rubber molecules. Boswell (*India-Rubber J.*, **64**, 981, 987 (1922)) and his students investigated the phenomenon of oxidation of rubber and obtained different oxidation products for each oxidizing agent. A solution of rubber in carbon tetrachloride oxidized by means of potassium permanganate in the absence of air (in carbon dioxide) gave a product of the formula, $C_{25}H_{40}O$, which in turn was readily oxidized in air to $C_{25}H_{40}O_2$. Using 3% hydrogen peroxide as an oxidizing agent, Boswell obtained a product with the formula, $C_{30}H_{49}O$, which in turn was easily oxidized to $C_{25}H_{40}O_2$.

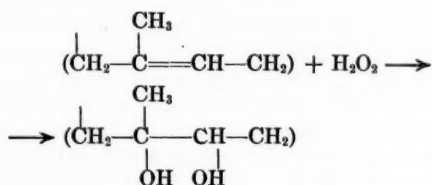
Rubber which had been exposed to direct sunlight was oxidized to $C_{10}H_{16}O$ by the action of air. By the action of a mixture of hydrogen peroxide and iodine, Boswell obtained $C_{25}H_{45}O_8I_2$.

In 1923, Pummerer and Burkard (*Ber.*, **55**, 3458) oxidized rubber by benzoyl hydroperoxide and obtained a rubber oxide $(C_6H_8O)_n$.

The majority of authors, with the single exception of Harries, have limited their work to obtaining the product of oxidation, and to the determination of its empirical formula by quantitative analyses for elements. This empirical formula does not give an opportunity to judge the character of the oxidation, the structure of the products of oxidation, or the structure of rubber.

The work of Robertson and Mair (*J. Soc. Chem. Ind.*, 41T (1930)) and later of Mair and Todd (*J. Chem. Soc. (London)*, **1932**, 386-399) is more interesting. In 1926, Robertson and Mair oxidized a benzene solution of rubber with permanganate in alkaline and neutral media, and obtained several products of oxidation which differed from one another in their physical properties and empirical formulas. The compounds obtained had compositions from $C_{10}H_{32}O_3$ to $C_{10}H_{48}O_{10}$, depending on the conditions and the proportion of oxidizing agent. Evidently during these tests, there was a splitting of the rubber molecule because, together with the high molecular compounds, there were obtained in large quantities from the products

of oxidation, low molecular compounds, such as formic acid, acetic acid, etc. By using hydrogen peroxide, Robertson and Mair obtained the products of oxidation in the form of amorphous powders, with the empirical formula $C_{29}H_{102}O_{16}$. The qualitative reactions of these powders for aldehyde and carboxyl groups gave negative results, which indicated that the compounds were polyhydroxy alcohols. The authors could not obtain the derivatives of alcohol from the amorphous powders, but using the method of Tzerevitinov and Chugaev, they determined the replaceable hydrogens, and found that all the oxygen which was absorbed by the rubber was in hydroxyl form. Based on these results, Mair and Todd assigned the following formula to the alcohol; $C_{50}H_{76}(OH)_{16}$. They decided that this alcohol was formed by means of a simple addition of the hydroxyl group at the places of double bond:



Comparing the work of Mair and Todd with the classic work by Harries, which deals with the oxidation of rubber by ozone, the former seemed to be a step toward the determination of the structure of the molecule of rubber. Harries obtained low molecular compounds—levulinic aldehyde, levulinic acid and others—which made it possible to draw only a scheme of the molecular structure of rubber, but which in no way gave the information necessary for determining the details of this structure.

The polyhydroxy alcohols obtained by Mair and Todd seemed to give some indication of the structure of the rubber molecule.

The method of Mair and Todd seemed to the authors of the present work a very attractive one for a comparative study of the products of oxidation of natural and sodium-butadiene rubber. These two rubbers differ first in the distribution of double bonds, secondly in the absence of the methyl group in one of them, and thirdly in the degree of polymerization.

The method of Mair and Todd is the one that assures the mildest conditions of oxidation, and therefore the authors used it as a basis for their work. Furthermore the authors thought that it would be of interest to study the products of oxidation of sodium-butadiene rubber and to compare them with the product of oxidation of light crepe, under identical conditions.

The authors decided to carry out the oxidation in sealed ampoules at constant temperature. By means of this method, the concentration of the rubber solution could be kept constant, and the combined oxidation by hydrogen peroxide and air could be excluded. Oxidation by air probably took place during the oxidation conditions used by Mair and Todd.

During the very first tests, it was suspected and later proved that the oxidation of sodium-butadiene rubber proceeds considerably slower and requires more time than that of natural rubber.

The conditions of the reaction were unquestionably mild, because the authors had not been able to detect the formation of tar or even a condition of becoming brown of the contents of the ampoules (both conditions were observed by Mair and Todd).

The separation and purification of the products of oxidation of sodium-butadiene rubber were carried out by the same methods as for the natural pale crepe, but very carefully controlled methods and conditions were necessary.

The solution of natural pale crepe in chloroform was oxidized by means of hydrogen peroxide in the presence of glacial acetic acid, and there was obtained a white amorphous powder. This powder was odorless, soluble in benzene, chloroform, alcohol, and acetone, and insoluble in ether and petroleum ether. When heated in a capillary tube at 70–80° it softened and began to decompose.

From the sodium-butadiene rubber under the same conditions was obtained an amorphous powder with a faint peculiar odor; it dissolved with preliminary swelling in methanol, ethanol, acetone, and pyridine; it was not soluble in benzene, anisole, ether, nor petroleum ether, but was slightly soluble in chloroform. Upon heating in a capillary tube at 70–80° it softened; at 115–120° it decreased in volume and became transparent, but did not melt. The elementary analysis of the products of oxidation gave the following results for natural pale crepe—found: C 65.14%, H 9.36%, O 25.51%; calculated for the formula $C_{10}H_{16}O_3$: C 65.2%, H 8.6%, O 26.1%. For sodium-butadiene rubber—found: C 68.3%, H 9.34%, O 21.95%; calculated for the formula C_4H_7O : C 67.7%, H 9.86%, O 22.4%. The difference between the results of the elementary analysis and the formula seemed to the authors reasonable on account of the extreme difficulties of purification of the products, which are not individual compounds, but a mixture of the products of different molecular weights.

The basic products in both cases were unsaturated hydrocarbons, therefore during the oxidation of such a hydrocarbon the degree of its unsaturation will change. A quantitative answer to this question was of special interest to the authors.

According to the results of Mair, Todd, Meerwein, and several other authors, oxidation with hydrogen peroxide of the unsaturated compound results in the addition of two hydroxyl groups to each double bond.

The present authors, however, have a contrary concept of the reaction. In the case of natural rubber, oxidation of the methyl group into a primary alcoholic group may be assumed, and besides, under the conditions of the experiment, there is a possibility of obtaining products of incomplete saturation of all double bonds. Accordingly the quantitative determination of the unsaturation has been a very important step in this work.

It was decided to use the method of hydrogenation as a means of identification of the products of oxidation, on account of the great difficulty of establishing their homogeneity.

With catalytic hydrogenation, the possibility of replacement was excluded, and therefore the authors decided to use those methods of catalytic hydrogenation which, according to the literature, would produce the best results. Replacement might also take place in the present case, as has been proved recently, and as the following experimental data will show.

The oxidation products of natural rubber after catalytic hydrogenation did not absorb hydrogen.

The products of oxidation of sodium-butadiene rubber, when subjected to hydrogenation, had been unquestionably hydrogenated, but the results were not concordant. Accordingly the authors could not draw any conclusions as to the number of double bonds remaining after oxidation. The so-called space difficulties which may easily be present in such high molecular compounds hinder catalytic hydrogenation. It was felt therefore that no conclusions regarding the satura-

tion of the oxidation products of pale crepe were justified, without checking these results. To this end, the original method of bromination of McKhiney was utilized. This method makes it possible to distinguish the replacement of hydrogen by bromine from the addition of bromine.

The results obtained with this method indicate that the oxidation product of pale crepe, $C_{10}H_{16}O_3$, is a saturated compound, and that the oxidation product of sodium-butadiene rubber, $C_{16}H_{28}O_4$, has one free double bond. The oxidation products of both rubbers were tested qualitatively for aldehydes. Neither product showed a mirror with an ammoniacal silver nitrate solution nor reduced Fehling solution. It is concluded, therefore, that the oxygen in the products of oxidation exists either in the form of hydroxyl, or in oxide form.

From the results it was clear that the product of oxidation of natural rubber, $C_{10}H_{16}O_3$, has only one hydroxyl group, *i. e.*, it is $C_{10}H_{15}(OH)O_2$, and that the product of oxidation of sodium-butadiene rubber, $C_{16}H_{28}O_4$, has only two atoms of oxygen in the form of hydroxyl groups. On the basis of the results of catalytic hydrogenation, bromination, determination of hydroxyl group and elementary analyses, the authors believe that the most reasonable formula for the product of oxidation of pale crepe is $C_{10}H_{15}(OH)O_2$; in other words, two oxygens have been added at the double bond, with formation of oxides. There is, in addition, an oxidation of the side methyl group to an alcoholic group.

In the case of sodium-butadiene rubber, the oxidation product, $C_{16}H_{28}O_4$, contains in all probability, two atoms of oxygen added in the form of hydroxides, two other atoms of oxygen as oxides, and one double bond remaining free. The latter agrees with the results of bromination. The possibility of the formation of a compound of the type, $C_{16}H_{26}(OH)_2O_2$, may therefore be assumed.

Elementary analysis of the oxidation products of natural rubber gave values which were very close to those of Mair and Todd, *i. e.*, about one per cent difference.

This slight difference cannot be taken as a proof that the products obtained are different from the products of Mair and Todd. It should be borne in mind that these workers dealt with a mixture of polymers, not with individual products, and that a slight change in the conditions may lead to a change in the ratio of the polymers.

It is interesting to note, however, that the results of the determinations of the unsaturation and the number of hydroxyl groups obtained in this work differ from the results of Mair and Todd.

Attention should be called to this fact, for Mair and Todd probably made several mistakes in their methods of determination, and as a result drew erroneous conclusions concerning the number of the hydroxyl group in the oxidation products, and also concerning the degree of unsaturation (the latter was determined by the method of regular bromination).

This seems more probable because, when the authors of the present work determined the amount of hydroxyls in pyridine by the method of Tzerevitinov and Chugaev, they obtained in several cases results which were close to the values of Mair and Todd. These results were discarded, as being obviously exaggerated on account of the hygroscopicity of pyridine (control test with benzoic acid).

The results of the bromination of Mair and Todd, according to their own statements, were higher than the theoretical values in the amount of bromine obtained. It is a well-known fact that during the bromination of unsaturated alcohols, besides the addition reactions, the reaction of replacement proceeds very easily. Regular bromination was accordingly not suitable in the present work. If the authors were to calculate the bromine number obtained in their experiments,

without deducting the amount of bromine consumed by replacement (determination with potassium iodate), their results would be very close to those of Mair and Todd.

A comparison of the products of oxidation of sodium-butadiene rubber and natural pale crepe led to the following very interesting conclusions:

1. The oxidation of sodium-butadiene rubber proceeds much more slowly than that of natural rubber.

2. The products have higher molecular weights than do the oxidation products of natural rubber, as judged by their slight solubility, their preliminary swelling in all solvents, and their appearance and behavior.

3. Judged by elementary analyses, the products of the oxidation of synthetic rubber involve addition to the basic hydrocarbon and have a lower degree of oxidation, than do the oxidation products of pale crepe.

In other words, in the case of oxidation of natural rubber, there are added three atoms of oxygen per two molecules of isoprene. In the case of the oxidation of sodium-butadiene rubber: there are added only two atoms of oxygen per two molecules of butadiene while for four molecules of butadiene one double bond is left unoxidized.

Experimental Part

The starting material for the oxidation of natural rubber was pale crepe. It was milled, was then extracted for 10–12 hours with acetone in a Soxhlet apparatus, was dissolved in benzene to make an approximately 7 per cent solution, was filtered by suction through a glass-wool filter in a carbon dioxide atmosphere, the filtered solution was precipitated with acetone, and the residue was again dissolved in benzene and reprecipitated. The rubber purified in this way was washed with acetone, dried in a vacuum desiccator and dissolved in chloroform. The concentration of chloroform solution was determined by evaporating a known weight of solution.

Synthetic rubber was prepared by means of the polymerization of rectified butadiene. The bomb with butadiene contained: butadiene 75.7%, acetaldehyde 0.06%, the residue 4.05%, and pseudo-butylene (*sym*-dimethylethylene) about 20% determined by difference (according to the analysis of the plant "Letter B"). Butadiene and small pieces of metallic sodium (1% of the weight of butadiene) were put in small ampoules, which were sealed and put into a shaker. During three days of shaking, the contents of the ampoules were transformed into a rubber-like mass, with small pieces of sodium. The ampoules were opened and volatile and liquid substances were removed *in vacuo*. After mechanical removal of the pieces of sodium, the synthetic rubber was purified in the same way as was the natural rubber.

After several preliminary oxidation tests under different conditions, following the basic principles of Mair and Todd, the best method of oxidation was found to be oxidation in sealed ampoules at a constant temperature. In this manner the concentration was certain to be constant, and the process could be carried out without interruption.

The same proportions of reagents as in the work of Mair and Todd were used, *viz.*, for each 25 grams of rubber, 55 cc. of 30% hydrogen peroxide, 250 cc. of glacial acetic acid, and 350 cc. of chloroform. The solution of rubber was poured into an ampoule (volume of ampoule 150–200 cc.) together with the acetic acid and hydrogen peroxide. In doing so part of the rubber was precipitated. The ampoule was sealed and put into an oven at a temperature of 43°. The ampoule

was shaken frequently. The rubber layer gradually disappeared, after some time two transparent layers were formed, and later a slight yellowish coloration appeared. At this stage the reaction was interrupted, the ampoules were taken out of the oven, and were opened. Upon opening the ampoules with sodium-butadiene rubber, the gaseous products were found, by means of barium hydroxide solution, to contain carbon dioxide.

To obtain the same effect when natural rubber was oxidized, 72–80 hours were necessary, and for synthetic rubber, 120–125 hours.

The oxidation product of light crepe was a slightly yellowish glassy mass, very easily ground to a powder. To purify it, it was dissolved in benzene and precipitated with petroleum ether. After several reprecipitations, an absolutely white amorphous powder was obtained. It then dissolved in alcohol with no turbidity.

When heated in a capillary tube at 78–83°, some droplets appeared, following which swelling occurred. After the chloroform solution was boiled away from the oxidation product of sodium-butadiene rubber, a brownish-yellow syrup with a peculiar odor (resembling the odor of poplar) remained in the flask. The addition of water precipitated a white, firm mass insoluble in benzene.

It was purified by dissolving in methanol and precipitating with sodium chloride. After several purifications, a white, amorphous, odorless powder was obtained.

The following results were obtained by determinations of the elementary composition (see the tables).

For the product of oxidation of natural rubber:

Sample	CO ₂	H ₂ O (in grams)	% C	% H	% O
0.1498	0.3578	0.1242	65.13	9.27
0.0992	0.2370	0.0846	65.15	9.54
0.1672	0.4002	0.1382	65.16	9.45
Average			65.14	9.35	25.51 by difference

For the product of oxidation of sodium-butadiene rubber:

Sample	CO ₂	H ₂ O (in grams)	% C	% H	% O
0.1524	0.3816	0.1290	68.34	9.49	...
0.1114	0.2830	0.0912	69.10	9.20	...
Average			68.72	9.34	21.95 by difference

Determination of the Number of Double Bonds

It was decided to use for this determination the method of catalytic hydrogenation. In the first tests hydrated palladium suboxide which had been precipitated on chalk was used as a catalyst. Ethanol was used as a solvent.

Preliminary experiments on the catalyst proved its satisfactory quality, *e. g.*, complete saturation of 0.5 gram of cinnamic acid was reached in 15 minutes, with 0.3 gram of catalyst.

For the hydrogenation of the oxidation product of natural rubber, the amount of catalyst was increased to 1 gram, but despite this increase, there was no appreciable hydrogenation. It was reasonable to suppose that the catalyst was poisoned by the substance. To prove this, during the course of one of the tests, after it was obvious that the reaction would not proceed, cinnamic acid was added to the reaction apparatus. The reaction started immediately after the apparatus was

shaken, and complete saturation was obtained after a short period of time. Therefore the catalyst was not poisoned.

The authors also tried hydrogenation by the method of Vilshteter, *i. e.*, palladium black in glacial acetic acid, and also by the method of Ginzberg, *i. e.*, with metallic palladium precipitated on powdered nickel. Both these methods gave negative results, in that no absorption of hydrogen was observed.

The same tests by the same three methods of catalytic hydrogenation of the oxidation product of synthetic rubber, showed that absorption takes place, and concordant quantitative results were not obtained. At the start, the hydrogenation was noticeable, but subsequently it became slower and proceeded very slowly for several hours.

Sample	The Amount of Catalyst	The Amount of Absorbed Hydrogen in Cc. (in grams)	Hours	Time		
				Hours	Minutes	
0.1215	0.13	19.6	3		22	The reaction was not finished
0.1206	0.22	10.7	1		50	
0.3680	0.37	19.6	3		45	
0.5806	0.19	29.0	1		10	

To determine the number of double bonds, it was necessary to resort to bromination. The potassium bromide-bromate method was not suitable under the conditions of the present test. Among several methods recommended in the literature, it was decided to use the method of McKhiney. The advantage of this method is that the amount of bromine which is consumed by addition to the double bonds may be determined separately from the amount of bromine consumed to replace hydrogen. (See the table below.)

The results with natural rubber showed that only replacement takes place, without any addition. It was therefore possible to draw a conclusion about the saturation character of the obtained product of oxidation of natural rubber. (See table below, second column.) The bromination of the product of oxidation of natural rubber:

Sample in Grams	The Amount in Cc. of 0.10 N Solution of Bromine That Was Used for:	
	Absorption	Replacement
0.2776	36.7	37.0
0.2570	33.9	30.0

The bromination of the product of oxidation of Na-butadiene rubber:

Sample in Grams	The Amount in Cc. of 0.10 N Solution of Bromine That Was Used for:			Bromine Number	The Amount of Bromine for C_4H_7O
	Absorption	Replacement	Addition		
0.2190	28.03	12.42	15.61	56.9	40.4
0.1522	17.76	5.73	12.03	63.2	41.8

Based upon these results with synthetic rubber, it is probable that for each group of C_4H_7O one-half atom of bromine is added, and for each $C_{16}H_{28}O_4$, two atoms of bromine are added.

Determination of the Number of Hydroxyl Groups

Neither oxidation product reacts with caustic alkali, or reduces ammoniacal silver nitrate solution, nor does either one reduce Fehling solution or fuchsin (sulphurous solution). It is concluded from these tests that the products must be

alcoholic, and therefore tests to determine the number of the hydroxyl groups were carried out by the method of Tzerevitinov and Chugaev.

In the first experiments with the oxidation product of natural rubber, pyridine was used as a solvent, but it was very difficult to handle because it is highly hygroscopic and forms a precipitate, which is the product of the reaction of pyridine with a magnesium organic compound. Therefore in subsequent tests, anisole was used as a solvent.

The following results were obtained:

The Solvent	Sample in Grams	The Amount of CH ₄ Produced, Corrected to the Normal Conditions, %	% OH
Pyridine	0.1372	23.17	11.97
Pyridine	0.0882	12.25	10.59
Anisole	0.1024	13.99	10.46
Anisole	0.1772	24.31	10.48
Anisole	0.1775	26.58	11.44
Anisole	0.1852	24.90	10.27

Average 10.83

For the formula $(C_{10}H_{16})_2O_2$ the percentage of OH is 9.24. Due to the fact that the product of oxidation of sodium-butadiene rubber was not soluble in isoamyl ether, xylene, or anisole, pyridine had to be used. Since, however, the product dissolved very slowly in pyridine, it was inconvenient to dissolve it in the Tzerevitinov apparatus. Accordingly the product was dissolved in pyridine in a 50-cc. calibrated flask and was left overnight. The other 50-cc. calibrated flask was filled with pyridine and also left overnight. The next day the amounts of liberated CH₄ in the blank-control sample of pyridine and in the solution of the product were determined. The pyridine was taken with a 10-cc. pipette.

A sample of 0.3094 gram was dissolved in 50 cc. of pyridine; therefore 10 cc. contained 0.0619 gram.

Determination No. 1 gave 10.70 cc. CH₄

Determination No. 2 gave 10.40 cc. CH₄

Average 10.6 cc. CH₄, or under normal conditions, 9.95 cc.

From this the percentage of OH was calculated to be 12.3%, while for the formula $C_{16}H_{26}(OH)_2O_2$ the amount of OH was 11.98%.

In conclusion we express our gratitude to M. I. Ushakov for his valuable aid.

The Hydrogenation-Cracking of Rubber

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In recent years the production of rubber has exceeded the demand, and in consequence there has arisen the problem of dealing with the surplus in the most suitable manner. There are a number of methods by which rubber may be converted into saleable commodities, but these are economic only if the raw material is surplus production and charged to the process at a cost much lower than that of rubber purchased in the normal market.

The manufacture of motor spirit from the surplus rubber is a possibility, and attempts have been made to produce a satisfactory spirit by the destructive distillation of rubber. The results obtained by this process, however, have not been promising, in that the spirit produced is very unstable and may contain as much as 80% of unsaturated hydrocarbons. It is therefore extremely difficult, if not impossible, to refine by the usual methods. Hydrogenation in the presence of catalysts offers a means of refining such a crude spirit, but it would seem a more satisfactory procedure to subject the rubber itself to hydrogenation-cracking. Waterman, Dewald, and Tulleners (*Erdöl u. Teer*, 22, 403 (1929); RUBBER CHEM. & TECH., 3, 33 (1930)) have already obtained some success with experiments in small discontinuous converters. They heated small quantities (150 g.) of first latex crepe in an autoclave at 450° for 15 minutes. In one experiment they used an initial pressure of hydrogen of 110 kg. per sq. cm., and in the other a pressure of 1 kg. per sq. cm.; the maximum pressures recorded in the two experiments were 250 and 50 kg. per sq. cm., respectively. The properties of the two liquid products are compared in the following table:

Initial pressure of hydrogen (kg. per sq. cm.)	110	1
C residue	0%	1.6%
Oil boiling below 220°	43.8%	39.9%
Bromine no.	40	34
n_D^{20}	1.45	1.46
Aniline point	21°	4°
Oil boiling 220-300°	23.5%	20.7%
Bromine no.	13	13
n_D^{20}	1.502	1.519
Aniline point	23.5°	4°

The better product was obtained from the experiments in which the rubber was treated in the presence of hydrogen under high pressure. The yields of both low-boiling and high-boiling oils were greater in this experiment, and though it is difficult to interpret the above results, the aniline points indicate that the influence of the high pressure of hydrogen was to produce a more saturated oil.

Preliminary Experiments in Discontinuous Converters

Experiments were first conducted on the same lines as those of Waterman and his co-workers; several different temperatures were, however, employed, and in some experiments a molybdenum catalyst was used. The pressure vessels were

mild steel converters of 2 liters capacity, as described by King and Matthews (*J. Inst. Fuel*, 6, 33 (1932)). A weighed quantity of rubber and of catalyst (when required) was introduced into a converter, and the latter was then charged with hydrogen to the required pressure and heated to reaction temperature at the rate of 4° per minute by means of gas flames. In order to effect adequate mixing of the contents of the converter, the latter was rotated horizontally throughout the heating period and for half an hour afterward. Finally the converter was allowed to cool overnight, the contents were discharged, and the oil product was fractionated.

The rubber used as the raw material in all experiments was a commercial crepe rubber. The catalyst used was a molybdenum catalyst prepared in the following manner: granular alumina gel ($\frac{1}{4}$ in. to $\frac{1}{8}$ in.) was boiled with an aqueous solution of a weighed quantity of ammonium molybdate, the whole being taken to dryness; drying was completed at 120° in an air oven. The dried material, which contained 25% of ammonium molybdate, was finally heated in air at 500° for 5 hours; in this way the ammonium molybdate was converted into molybdic oxide.

The experiments were carried out under the conditions which have been found most suitable for promoting hydrogenation. The conditions were: weight of rubber treated, 150 g.; initial hydrogen pressure, 120 atm.; time of heating at reaction temperature, 2 hours; amount of catalyst, 20% of the supported catalyst (equivalent to 5% of ammonium molybdate) together with 5% of sulfur. The sulfur was added in order to permit the formation, during the hydrogenation-cracking process, of molybdenum sulfide, which is the active catalyst.

A short series of experiments was carried out to determine the effect of varying the temperature from 375° to 450°. The results are set out in Table I.

The oil products obtained from Expts. 1, 2, and 3, in which the catalyst was used, were all almost colorless, though that made at a reaction temperature of 375° (Expt. 1) was tinted yellow. The yield of spirit to 200° increased as the reaction

TABLE I
PRELIMINARY EXPERIMENTS IN DISCONTINUOUS CONVERTERS

	Experiments with Catalyst			Experiments without Catalyst	
No. of experiment	1	2	3	4	5
Reaction temperature	375°	400°	450°	400°	450°
Final pressure, atm.	102	88	78	115	101
Yield of product (% by wt. of rubber):					
Liquid	98.5	99.1	79.3	94.0	86.3
Gas + loss	1.5	0.9	20.7	6.0	13.7
Color of liquid product	Pale yellow	Water-white	Water-white	Dark brown	Orange-red
Fractionation of liquid product (% by wt. of rubber):					
Up to 100°	4.0	6.6	19.2	6.1	11.1
100-170°	11.4	17.7	32.1	16.7	24.2
170-200°	8.1	10.3	8.2	12.2	10.9
200-230°	4.2	9.4	5.8	6.2	6.9
230-270°	10.4	13.2	3.4	11.5	9.6
270-300°	9.9	10.3	3.0	9.1	6.2
Residue	48.1	28.8		30.5	11.7
Loss	2.4	2.8	7.6	1.7	5.7
Total	98.5	99.1	79.3	94.0	86.3
Nature of residue	Brown viscous oil	Pale yellow viscous oil	Brown mobile oil	Black viscous tar	Black viscous tar

temperature rose; it was 23.5% at 375°, 34.6% at 400°, and 59.5% at 450°. Very little gas was formed at 375° or 400°, but at 450° about 20% of the original rubber appeared in the products as gas. The residues at 300° from the fractionation of the liquid products were all clear oils, the viscosity diminishing with rising reaction temperature; the residue from Expt. 1 (reaction temperature 375°) was of the consistency and appearance of lubricating oil.

The amount of hydrogen absorbed by the rubber was not calculated, but a measure of it is given by the final pressure in the converter. This was 102 atm. in Expt. 1 (reaction temperature 375°), 88 atm. in Expt. 2 (400°), and 78 atm. in Expt. 3 (450°); the absorption of hydrogen thus increased as the temperature of reaction was raised and at 450° was of the order of 4-5% by weight of the original rubber.

The amount of hydrogen absorbed by the rubber was much less in the absence of catalyst; at 400° the final pressure was 115 atm. in Expt. 4 as compared with 88 atm. in Expt. 2; at 450°, the final pressures were, respectively, 78 and 101 atm. in the experiments with and without catalyst. The catalyst was therefore very effective in promoting the hydrogenation of the rubber.

The yield of spirit to 200° from Expt. 4, in the absence of catalyst was 35%. Approximately the same yield (34.6%) was obtained from Expt. 2 at the same reaction temperature (400°), but in the presence of the catalyst. Whereas, however, the spirit from Expt. 2 was a stable, water-clear spirit, that from Expt. 4 rapidly darkened in color and deposited gum. A similar influence of the catalyst was observed in Expts. 3 and 5 at 450°. Finally the residues at 300° from the fractionation of the liquid products obtained in the absence of catalyst showed a marked difference in nature from those obtained in the presence of catalyst; the latter were clear oils whereas the former were black viscous tars. It would appear that the principal action of the catalyst consisted in the hydrogenation of the molecules or fragments of molecules produced by the decomposition of the complex rubber molecules.

It was found that the fraction boiling above 200° of the oil product dissolves rubber fairly readily, and that a 50% solution of rubber in this oil could be made without much difficulty. A method of operating a continuous process for the hydrogenation of rubber was therefore indicated and it was considered desirable to investigate its practicability. With this end in view, a stock of liquid product was obtained by hydrogenating about 50 pounds of rubber (two experiments) in a large converter of 50 liters capacity. A batch of about 25 pounds of rubber with the catalyst was charged into the converter and hydrogen was pumped in to a pressure of 200 atm. The temperature was gradually raised to 420°, and hydrogen was passed at 200 atm. pressure so as to remove the greater part of the product as vapor. The yield of distillate obtained in this way was 89% by weight of the original rubber, and the residue in the converter was 4%; the distillate was a clear, pale yellow oil (d_{15}^{20} 0.862) and the residue was a dark brown, viscous oil of the consistency of treacle.

The distillate was topped to 200°, giving 34% of spirit to 200°. Sufficient rubber was then added to the residue to make a 50% solution and the mixture was re-fluxed until the rubber was completely dissolved. The resulting solution, a dark brown viscous oil having d_{15}^{20} 0.906, was used with 1% of dissolved sulfur as the raw material in the subsequent continuous experiments.

Experiments in a Continuous Plant

The apparatus used in the continuous experiments has been described elsewhere (King and Cawley, *Fuel Research Tech. Paper*, No. 41. In the press). It consists

essentially of an electrically heated reaction vessel, into the top of which oil and hydrogen are fed at 200 atmospheres' pressure. The reaction vessel is filled with the supported molybdenum catalyst (500 ml.) through which the mixed oil vapors and gas pass downward to an outlet at the base of the vessel. Thence they pass through a water-cooled condenser into a separator. The residual gas leaves at the top of the separator through a needle valve, at which its pressure is reduced to atmospheric, and passes to a flow meter for controlling the rate of passage, an iron oxide purifier, a meter, and finally a gas-sample bottle by means of which an average sample can be collected over any period of time. The liquid product is released at half-hourly intervals from the bottom of the separator through a needle valve to an atmospheric-pressure receiver, whence it is withdrawn, weighed, and its specific gravity measured every hour; the dissolved gas evolved at the same time passes through a caustic soda wash-bottle and a meter and is collected in a holder. A thermocouple pocket through the center of the reaction vessel enables the temperature at the top, center, and bottom of the catalyst bed to be measured by means of a three-junction thermocouple.

The conditions of operation were as follows: (a) the reaction pressure was 200 atm.; (b) the reaction temperature was varied from 360° to 480° in different runs; (c) the rate of residual gas, by which the input of hydrogen is controlled, was 5 cu. ft. per hour; (d) the throughput of rubber solution was 220–250 ml. per hour. In starting an experiment, the hydrogen was pumped in to a pressure of 200 atmospheres, the hydrogen and oil flow was begun, the electric heaters were switched on, and the catalyst bed was gradually raised to the reaction temperature. When steady conditions were reached, the liquid products were collected. The products were collected over "periods" of 12 hours; specific gravities of the hydrogen, residual gas, and dissolved gas were measured so that a complete weight balance over each period was obtained. In addition all the gases were analyzed in order that the hydrogen absorptions could be calculated. Each period sample of liquid product was fractionated, and its specific gravity determined.

Experiments at various temperatures were carried out under the above conditions. The product obtained at 480° had the appearance of a water-clear spirit. On lowering the reaction temperature the products became less clear in appearance and more viscous. The products obtained at 450° and lower temperatures were turbid, mobile oils which deposited, on keeping, a small amount of a white flocculent precipitate which was not identified. The yield and specific gravity of the oil products, and the amount of spirit to 200°, are recorded in Table II. Full results are given in Tables VIA and VIB; Table VIA contains the results of the examination of the liquid products, and Table VIB the weight balances and hydrogen absorption data.

TABLE II

Period	Reaction Temperature	d_{40}^{20} of Total Oil Product	Yields, Per Cent by Wt. of Original Rubber Solution, Spirit to 200°	
			Total Oil Product	Spirit to 200°
1	450°	0.805	96.1	42.9
2	480°	0.764	81.1	63.0
3	400°	0.854	98.8	19.7
4	390°	0.861	99.0	17.9
5	380°	0.868	98.0	13.8
6	370°	0.874	98.6	10.6
7	360°	0.883	99.0	8.7
8	450°	0.807	94.6	42.9

The first temperature investigated was 450°. A high yield of liquid product

was obtained and there was very little gas formation. The yield of spirit to 200° was 42.9%.

The reaction temperature was raised to 480° (Period 2), and the yield of spirit to 200° was then 63.0%. This increased yield of spirit, however, was obtained only at the expense of converting a considerable quantity of the raw material into gas. The total yield of oil product was only 81.1% and the amount of the original material converted into gas must therefore have been of the order of 15%. It is considered that the optimum temperature for the conversion of rubber into spirit is within the range 450° to 480°, though if there is no objection to gas production, an increased rate of production of spirit could probably be obtained at 500°.

The production of spirit to 200° at temperatures from 400° to 360° fell gradually from 19.7 to 8.7%. The oils boiling above 200° were fairly viscous, yellow oils which deposited a brown, flocculent precipitate (not identified) on keeping.

By reference to Table VIb the data for the absorption of hydrogen at the various temperatures of reaction may be seen. The absorption of hydrogen decreased steadily from 3.88% by weight of the original raw material at 480° to about 1.9% at 360–390°. The hydrogen evolved as gaseous hydrocarbons was 2.80% at 480°, 1.33% at 450°, and 0.3 to 0.5% at 360–400°. There was thus a marked decomposition to gaseous hydrocarbons between 450° and 480°.

After Period 7 (360°) the temperature for Period 8 was raised again to 450°, that is, the reaction temperature of Period 1. It was found that the product obtained from Period 8 was practically identical with that from Period 1; the specific gravity and yield of spirit to 200° were 0.807 and 42.9% for the former as compared with 0.805 and 42.9% for the latter. It is concluded that the rate of deterioration of the catalyst is very slow at low temperatures of reaction (360–400°); experience with the treatment of tar suggests that the rate of deterioration would probably be greater at higher temperatures of reaction (about 480°).

Motor Spirit.—All the spirits made at the different reaction temperatures were stable, water-clear spirits. The spirit to 170° was analyzed by the Manning method (*Fuel Research Technical Paper*, No. 28 (1930)); the total motor spirit fraction (boiling up to 200°) could not be analyzed as the method is applicable only to readily vaporizable spirits. The results of the analysis are given in Table III.

TABLE III

Period	1	2	3	4	5	6	7
Reaction temperature	450°	480°	400°	390°	380°	370°	360°
Analysis of spirit boiling up to 170°, % by wt.:							
Aromatic hydrocarbons	14.5	17.2	14.2	14.2	11.7	9.4	10.7
Unsaturated hydrocarbons	1.3	1.5	1.1	1.4	2.9	2.6	1.4
Saturated hydrocarbons	84.2	81.3	84.7	84.4	85.4	88.0	87.9

The analysis of the spirits shows them to contain only 1 or 2% of unsaturated hydrocarbons, and since the method of analysis is accurate only to $\pm 1\%$, it is not certain that they contain even that amount. The spirits consist largely of saturated hydrocarbons with small quantities of aromatic hydrocarbons; there is a slight tendency for the aromatic hydrocarbons to decrease and the saturated hydrocarbons to increase as the temperature of reaction is lowered. It is to be expected, therefore, that the spirits would require very little, if any, refining in order to render them suitable for use as motor spirit.

All the yields quoted above refer to one passage of the rubber solution over the catalyst. The oil boiling above the motor spirit range is used for making up the rubber solution used as the raw material for the process. The latter can thus be adjusted to produce motor spirit only.

In Expts. 1 and 2 at 450° and 480°, respectively, in which the total yields of oil product were, respectively, 96.1 and 81.1% by weight of the original rubber solution, the yields of the various fractions were:

	480°	450°
Spirit to 200°	63.0	42.9
Oil 200-300°	13.6	41.3
Oil > 300°	4.5	11.9
Total	81.1	96.1

In a commercial process the choice of temperature would be influenced by considerations of total yield, throughput, and nature of product desired. At 480° the yield of oil would be lower owing to the greater degree of cracking to gaseous hydrocarbons, and there would be insufficient high-boiling oil produced to enable further raw material to be prepared. The lower temperature would therefore appear to be the most practicable.

TABLE IV

Lubricating Oil	Fraction from Rubber	Poor Quality Petroleum Oil	Good Quality Petroleum Oil I	Good Quality Petroleum Oil II
d_{25}^4	0.916	0.949	0.880	0.927
Aniline point	77°	67°	113°	80°
Loss in wt. after 24 hours' heating at 150°	7%	6%	1%	8%
Viscosity at 25° ^a	4.05	4.86	3.11	2.79
Viscosity at 50° ^a	0.602	0.726	0.701	0.532
Viscosity at 75° ^a	0.173	0.205	0.238	0.171

^a Poises.

Lubricating Oils.—In view of the appearance of the hydrogenated oils boiling above 200°, it was considered desirable to examine their suitability for use as lubricants. A preliminary experiment was carried out at 350° in a 2-liter converter, the heating at reaction temperature being continued for 4 hours. The liquid product was filtered and topped to 200°. The residue, a greenish yellow oil, was fractionated at 4 mm. pressure in a small stream of nitrogen and the fraction boiling from 200° to 300° was collected. This fraction, which amounted to 13% by weight of the rubber, was a pale yellow oil with a green fluorescence and a slight odor of rubber, and though quite clear when first prepared, it deposited a slight, flocculent brown precipitate after keeping for some weeks.

TABLE V

Reaction Temp.	Total Yield of Oil Boiling Above 200° at 760 Mm., % by Wt. of Raw Material	Fractionation of Oil Boiling Above 200°: of Raw Material			Per Cent by Wt.	
		200°/760 Mm.—195°/4-5 Mm.	195-260°/4-5 Mm.	260-320°/4-5 Mm.	Residue at 320°/4-5 Mm.	
Vehicle	50	43.8	5		1.2	
450°	51.1	End b. p. 170°/4-5 mm.	
400°	79.1	54.6	14.7	2.5	7.3	
390°	80.7	51.8	15.3	6.0	7.6	
380°	83.9	49.6	14.3	6.7	13.3	
370°	87.6	46.7	14.5	7.0	19.4	
360°	90.1	46.2	14.9	6.7	22.3	

The oil was subjected to an oxidation test by heating for 24 hours in air at 150°. By this treatment it lost 7% by weight, but the residue after heating was a clear oil, though darker in color than the original oil; it was not sticky or gummy, and contained only traces of pitch. The properties of the oil are shown in Table IV in comparison with those of some petroleum lubricating oils.

It was concluded from the density, aniline point, and stability to oxidation that the viscous oil obtained by the hydrogenation of rubber would be suitable for use as a lubricant. The viscosity of the oil is the least satisfactory property; the viscosity-temperature gradient is steeper than that of a good-quality petroleum oil, although very similar to that of a poor-quality petroleum oil from an aromatic-paraffinous base petroleum.

In order to determine the optimum temperature for the production of this viscous oil in a continuous process, the products from the continuous experiments at the various reaction temperatures were examined. They were distilled at atmospheric pressure to remove spirit boiling below 200°, and the residues were fractionated under reduced pressure in a stream of nitrogen to determine the yield of the lubricating fraction. The vehicle, that is, the fraction of the hydrogenated-rubber oil boiling above 200° which was used in preparing the raw material for the continuous experiments, was also examined. The results are recorded in Table V.

The fractions collected during the distillation under reduced pressure were: (a) 200°/760 mm. to 195°/4-5 mm.; (b) 195-260°/4-5 mm.; (c) 260-320°/4-5 mm.; (d) residue.

The first of these fractions (a) was produced in gradually diminishing quantity (from about 55 to 46% of the raw material) as the temperature of reaction decreased from 400° to 360°. The oil was mobile and of a faint yellow color. Judging from the small quantities of aromatic hydrocarbons present in the spirit boiling up to 200°, it may be assumed that fraction (a) is also comparatively free from aromatics and hence suitable for use as Diesel fuel.

The second fraction (b) was produced in approximately equal amount (14 to 15%) at all reaction temperatures from 400° to 360°; it was entirely absent from the product made at 450°. The oil was viscous, and when first produced was clear and colored pale yellow with a slight fluorescence. On keeping, however, it became turbid and deposited a small amount of a brownish white, flocculent precipitate.

The third fraction (c) was present to the extent of 2.5% in the product made at 400°, but otherwise the amount (6 to 7%) was approximately the same at all reaction temperatures. The fraction was a viscous, yellow oil which became turbid when cold and possessed a gel-like appearance.

The residue (d) had the appearance of a gel. It was clear, yellowish green in color and just able to flow at room temperature. Both the residue and the third fraction (c) deposited, on keeping, the flocculent precipitate observed in most of the rubber oils. The yield of the residue increased with decreasing reaction temperature at the expense of the oils boiling below the lubricating oil range.

Thus at 400° there was a total yield of about 17% of viscous oils in the lubricating oil range; this amount increased to 21% at 390° and remained approximately unchanged down to 360°. It is possible, however, that the thick residue could be further distilled to yield a fair proportion of more viscous lubricating oil. By the fractionation of the vehicle, 5 to 6% (by weight of the raw material) of viscous oil was obtained; the oil was much darker in color than that produced in the continuous hydrogenation experiments. It would thus appear that the net yield of viscous oils in the lubricating oil range from the continuous experiments was 15%

TABLE VIA
EXAMINATION OF LIQUID PRODUCTS
On Crude Dry Product

Basis of Calculation: Per Cent by Wt.									
Period	Temperature	1 450°	2 480°	3 400°	4 390°	5 380°	6 370°	7 360°	8 450°
Water ^a		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Oil		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Total product		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
<i>d</i> ₁₅ of product		0.805	0.764	0.854	0.861	0.868	0.874	0.883	0.807
Fractionation of neutral oil:									
Up to 100°		8.5	22.1	10.3	9.7	6.4	4.5	3.4	9.4
100-170°		22.2	40.7	9.6	8.4	7.6	6.3	5.3	21.3
170-200°		13.9	14.6	7.9	7.2	5.7	4.8	4.7	14.6
200-230°		16.1	8.8	17.5	15.9	15.0	13.9	13.0	14.5
230-270°		14.8	6.4	11.8	12.0	11.2	10.9	12.0	18.1
270-300°		12.1	3.0	42.8	46.6	53.8	59.3	61.3	8.5
Residue		10.2		0.1	0.2	0.3	0.3	0.3	12.6
Loss		2.2	4.4						1.0
Total		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Basis of Calculation: Per Cent by Wt.					On Original Raw Material				
Period	Temperature	1 450°	2 480°	3 400°	4 390°	5 380°	6 370°	7 360°	8 450°
Water ^a		1.2	1.4	1.4	1.0	1.1	1.1	0.7	1.0
Oil		96.1	81.1	98.8	99.0	98.0	98.6	99.0	94.6
Total product		97.3	82.5	100.2	100.0	99.1	99.7	99.7	95.6
<i>d</i> ₁₅ of product		0.805	0.764	0.854	0.861	0.868	0.874	0.883	0.807
Fractionation of neutral oil:									
Up to 100°		8.2	18.0	10.2	9.6	6.3	4.4	3.4	8.9
100-170°		21.4	33.1	9.5	8.3	7.5	6.2	5.3	20.2
170-200°		13.3	11.9	7.8	7.1	5.6	4.7	4.6	13.8
200-230°		15.5	7.2	17.3	15.7	14.7	13.7	12.9	13.7
230-270°		14.2	5.2	11.7	11.9	11.0	10.7	11.9	17.2
270-300°		11.6	2.4	42.3	46.1	52.6	58.5	60.7	8.1
Residue		9.8		0.0	0.3	0.3	0.4	0.2	11.9
Loss		2.1	3.3						0.8
Total		96.1	81.1	98.8	99.0	98.0	98.6	99.0	94.6

^a Formed mostly from small amounts of carbon monoxide and carbon dioxide in the "hydrogen."

TABLE VII.—WEIGHT BALANCES AND MISCELLANEOUS DATA
Weight of Catalyst = 500 G.

Period	1	2	3	4
Temperature	450°	480°	400°	390°
Rate of ingoing hydrogen (approx.), cu. ft./hr.	6.5	8	6.5	6.5
Rate of residual gas (approx.), cu. ft./hr.	4	5	5	5
Rate of oil feed (approx.), cc./hr.	220	220	220	250
Weight balance (calc. on 100 g. raw material):				
Ingoing materials:				
Oil (dry), g.	100.0	100.0	100.0	100.0
Hydrogen { Cu. ft. at 60° F. and 30 in.	3.33	3.90	3.23	2.86
{ S.g. (air = 1)	0.098	0.098	0.098	0.098
G.	11.3	13.2	10.9	9.7
Total, g.	111.3	113.2	110.9	109.7
Outgoing products:				
Liquid product (dry), g.	96.1	81.1	98.8	99.0
Water, g.	1.2	1.4	1.4	1.0
Residual { Cu. ft. at 60° F. and 30 in.	2.15	2.39	2.36	2.10
gas { S.g. (air = 1)	0.134	0.173	0.115	0.116
G.	9.8	14.4	9.4	8.4
Dissolved { Cu. ft. at 60° F. and 30 in.	0.18	0.39	0.11	0.09
gas { S.g. (air = 1)	0.707	1.023	0.473	0.408
G.	4.4	13.8	1.7	1.3
Loss, g.	-0.2	2.5	-0.4	0.0
Total, g.	111.3	113.2	110.9	109.7
Analysis of gases:				
CO ₂ , %	0.3	0.5	0.8	0.4
C ₂ H ₄ , %	0.1	0.2	1.3	nil
CO, %	0.2	0.3	0.3	0.4
H ₂ , %	93.3	92.1	95.1	94.1
C ₂ H ₆ , %	5.1	5.2	2.4	3.3
N ₂ , %	1.0	1.7	1.3	1.8
n	1.31	1.41	1.19	1.26
Hydrogen absorption data (% by wt. of the raw material):				
Hydrogen absorbed	3.00	3.88	2.20	1.95
Hydrogen evolved as water in the product	0.13	0.16	0.16	0.11
Hydrogen evolved as gaseous hydrocarbons	1.33	2.80	0.48	0.54
Hydrogen absorbed, net	1.54	0.92	1.56	1.30

0.48
0.54
1.300.48
1.562.80
0.921.33
1.54

Hydrogen evolved as gaseous hydrocarbons

Hydrogen absorbed, net

Period Temperature	5 380°	6 370°	7 360°	8 450°
Rate of ingoing hydrogen (approx.), cu. ft./hr.	6.5	6.5	6.5	7.0
Rate of residual gas (approx.), cu. ft./hr.	5	5	5	4.5
Rate of oil feed (approx.), cc./hr.	240	240	220	230
Weight balance (calc. on 100 g. raw material):				
Ingoing materials:				
Oil (dry), g.	100.0	100.0	100.0	100.0
Hydrogen { Cu. ft. at 60° F. and 30 in. S.g. (air = 1)	2.96 0.098	2.86 0.098	3.22 0.098	3.30 0.098
Total, g.	110.0	109.7	110.8	111.2
Outgoing products:				
Liquid product (dry), g.	98.0	98.6	99.0	94.6
Residual { Cu. ft. at 60° F. and 30 in. S.g. (air = 1)	2.22 0.121	2.17 0.117	2.34 0.116	2.32 0.135
Dissolved { Cu. ft. at 60° F. and 30 in. S.g. (air = 1)	0.10 0.309	0.07 0.265	0.14 0.254	0.19 0.514
Loss, g.	1.1 0.5	0.6 0.7	1.2 0.5	3.3 1.4
Total, g.	110.0	109.7	110.8	111.2
Analysis of gases:				
CO ₂ , %	0.3	0.4	0.4
C ₂ H ₄ , %	nil	0.1	nil
CO, %	1.2	0.8	0.2
H ₂ , %	96.0	93.1	96.9
C ₂ H ₆ , %	1.5	3.9	1.3
N ₂ , %	1.0	1.7	1.2
n	1.66	1.28	1.35
Hydrogen absorption data (% by wt. of the raw material):				
Hydrogen absorbed	1.84	1.84	1.95
Hydrogen evolved as water in the product	0.12	0.12	0.08
Hydrogen evolved as gaseous hydrocarbons	0.30	0.54	0.26
Hydrogen absorbed, net	1.42	1.18	1.61

by weight of the raw material. Since the raw material used in these experiments was a mixture of equal weights of rubber and vehicle, the yield of viscous oil from the rubber was 15 to 30% by weight of the rubber; the higher figure is probably nearer the correct yield since it is unlikely that any appreciable quantity of viscous oil would be produced from the vehicle apart from that already present.

Conclusions

Rubber is amenable to treatment by the process of hydrogenation-cracking at a pressure of 200 atmospheres of hydrogen and at temperatures above 360°. The rubber is suitably treated in a continuous plant in the form of a solution containing 50% of rubber and 50% of an oil boiling above 200° obtained by the hydrogenation of rubber.

At a reaction temperature of 450–480°, and in the presence of a molybdenum catalyst, a high yield of spirit (boiling up to 200°) is obtained. In one passage of the raw material over the catalyst the yield is from 40 to 60% by weight of the rubber solution, the remainder being oil (53 to 18%) and gaseous hydrocarbons. The crude product is a pale yellow mobile oil, and the fraction boiling below 200° a water-clear spirit. The latter contains aromatic 15, unsaturated 1.5, and saturated hydrocarbons 83.5%. It therefore requires only very little refining to make it stable on storage.

As the reaction temperature is lowered, the yield of spirit decreases, while that of high-boiling oil increases. The high-boiling oil also becomes more viscous. Thus at 370° the yields, as percentages by weight of the rubber solution, are: spirit boiling up to 200° 10.6%, and oil boiling above 200° 87.6%. The latter is distilled to produce 46.7% of Diesel oil, 21.5% of lubricating oil, and 19.4% of residue. The greater part of the Diesel oil and the high-boiling residue is required to prepare rubber solution for use as the raw material.

Rubber can therefore be treated by a hydrogenation-cracking process to yield either motor spirit alone or motor spirit, fuel oil, and lubricating oil, depending on the temperature of treatment. As a commercial project the rubber treated would require to be surplus production available to the process at a much lower cost than that of rubber purchased in the normal market.

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The Chlorination of Disaggregated Rubber

B. V. Buizov, V. S. Molodenskii, and N. I. Mikhailov

The thoughts of rubber chemists have of late been turning to the use of rubber as a raw material to obtain chemical derivatives which, in turn, may be used in lacquers and as plastic masses. This has come about partly by the enormous production of rubber, and also by the demand of industry for substances which are stable to corrosive agents, and may be used for surfacing solid materials. Having lost their most basic property, *viz.*, elasticity, derivatives of rubber have acquired new qualities, that is, those of saturated chemical compounds.

It is quite natural that during the process of formation of chemical derivatives of rubber, the structure of the latter cannot be preserved, and its elasticity is destroyed. To obtain chemical derivatives of rubber, it is necessary not only to forego attempts to preserve the elastic structure of rubber, but also to take all possible means to destroy the elasticity. Only a product which has lost its elastic structure can be conveniently subjected to chemical treatment.

In our previous work (cf. *Kautschuk*, 10, 86, 104 (1934)) we have shown that the only rubber which can be subjected to oxidation is rubber which has lost its elastic structure; and we also made the statement that in the initial period of aging (aging under the influence of copper compounds), disaggregation of the rubber takes place, thus opening a wide field for the oxidation process. We proved experimentally that, even under the influence of copper compounds, there is no oxidation of rubber during the first stages of the process.

Accordingly, agents which promote the aging of rubber and thus destroy permanently its structure are necessary agents of the preliminary stage of chemical treatment of rubber.

With this as a concept, we started an investigation to obtain chemical derivatives from a disaggregated product, and have proved the correctness of our point of view.

A method of obtaining chlororubber to which attention should be called is the patented process of the I. G. Farbenindustrie (cf. *India Rubber Journal*, 86, 145, 1933), which is based on the preliminary action of "oxidizing" reagents on latex, including certain copper salts. The authors of the patent mention the property of latex to form upon chlorination, a stable product, as a result of the chlorination of *oxidized* rubber. We believe that in this case it is not correct to talk about *oxidation*, but rather about a disaggregation of the rubber, because oxidized rubber does not yield a good chlorination product. In the present paper we have described only the results of our investigations on the formation of chlorinated rubber by means of the chlorination of disaggregated raw material.

To chlorinate the rubber, we dissolved the preliminary treated samples of rubber in chloroform, and subjected 100 cc. of solution to the action of dry chlorine at room temperature for different lengths of time. Afterward the solution was shaken with calcium oxide, filtered, and the chlororubber was precipitated from the filtrate with benzene and was dried at a constant temperature of 85° C. The effects of temperature and ultra-violet light on the product were then investigated. It was analyzed for its chlorine content by fusion (0.2-0.3 g.) with a mixture of

KNO₃ and NaOH, dissolving the fusion mixture, neutralizing with HNO₃ and determining the chlorine volumetrically.

The solutions of non-disaggregated rubber (the samples were not previously treated) were chlorinated very slowly, following literature statements and practice. After 30 minutes of chlorination, the chlorination product, containing up to 20% Cl, was precipitated from the solution with petroleum ether. This product still had some elasticity, was easily ignited, was quickly decomposed upon heating, and its film, when put on a copper plate and subjected for one hour to ultra-violet radiation, was unstable.

A sample of smoked sheet, which had been subjected for one year to the destructive action of 0.1% CuCl₂, was introduced into the rubber during milling. This sample had lost its elasticity completely, being transformed into a semi-liquid paste.

A three per cent solution of this "rubber" in CHCl₃ was prepared, and the solution was subjected to dry chlorine for different periods of time. The chlorination started immediately after the first passing of chlorine.

The products of chlorination had the following chlorine contents in relation to the time of chlorination:

No. of Sample	The Period of Chlorination	Per Cent Chlorine in Product	The Stability of Product during the Ultra-violet Test
1	3 min.	27.5	Not stable
2	5 min.	32.9	Not stable
3	10 min.	42.1	Weakly stable
4	15 min.	44.8	After 4 hrs. of irradiation gave the reaction of disaggregation
5	20 min.	51.1	Ten hrs. of irradiation did not decompose these products
6	30 min.	51.2	
7	1 hour	51.2	

Products 1, 2, and 3 were green solid brittle masses; product 4 was a brittle and slightly yellow mass. Products 5, 6, and 7 were either white powders, or white porous flaky substances. Accordingly rubber is disaggregated by means of copper chloride, becomes very active at chlorination, and gives products with a constant amount of chlorine after a period of 20 minutes of chlorination. It is identical to a chlororubber. This, on one hand, gives the key to develop a better method of obtaining chlororubber and, on the other hand, strikingly confirms our theory concerning the character of the action of copper compounds on rubber, which has been discussed in the work above mentioned. These results necessitated our undertaking a complete series of tests of the chlorination of disaggregated rubber.

To start these tests, we added copper chloride during the milling of rubber (smoked sheet). The sample was then dissolved in chloroform, and the resulting 3% rubber solution was chlorinated. As we expected, after 30 minutes of chlorine action this sample did not give chlororubber. The disaggregating action of salts of copper requires a certain definite time. The beginning of disaggregation is shown by the appearance of stickiness in the sample. The freshly milled sample does not answer these requirements.

We had kept such a sample of smoked sheet at a constant temp. of 100° for 4 hours, and after that we made a 3% solution in chloroform, and subjected it to chlorination. After 20 minutes of chlorination, a product was obtained which had a slightly yellowish shade, containing 50.0% chlorine. It should be mentioned that after 4 hours' exposure, the rubber to which was added copper chloride at a temperature of 100° formed a sticky pasty product, which is the product of disaggregation of rubber.

We disaggregated the rubber by 2 methods: in solution with copper oleate and by the action of ultra-violet radiation.

The solution of rubber, which was subjected for 4 hours to the action of copper oleate (1% on the rubber) gave, after 15 minutes of chlorination, a product which contained 51.2% chlorine. The chlorine content in the product did not increase noticeably upon further chlorination.

A freshly prepared rubber solution containing copper oleate did not show such activity upon chlorination, and gave a product which was semi-elastic and had a low content of chlorine.

On the contrary, a freshly prepared rubber solution which contained copper oleate, and which was subjected to 6 hours of ultra-violet radiation gave a good white powdery or flaky product containing after 15-20 minutes of chlorination, 50.9% chlorine.

A freshly prepared solution of rubber free of copper compounds was subjected to 6 hours of ultra-violet radiation. After chlorination for 30 minutes, this rubber gave a slightly yellowish product, containing 53.9% chlorine. After longer chlorination, *viz.*, 40-50 minutes, the chlorine content increased to 68.2%.

Special importance should be paid to the fact that when the rubber was disaggregated by means of copper compounds and then chlorinated, the product of chlorination contained up to 51% Cl. This indicates that the molecule of this product has 2 atoms of chlorine per five atoms of carbon, and its formula must be $C_5H_6Cl_2$. On the other hand, the chlorinated product of the rubber, which was not subjected to the action of copper compounds, contained up to 68% of chlorine and had an empirical formula $C_5H_6Cl_4$. These facts, and also the fact (according to our preliminary experiments) that copper compounds do not produce a profound disaggregation of sodium-butadiene (alcoholic) rubber, confirms our hypothesis about the mechanism of disaggregation of natural rubber by copper compounds.

Probably this disaggregation proceeds through the formation of cyclic compounds of rubber, and this is impossible for sodium-butadiene rubber because the methyl group is absent in its molecule. As a result of the formation of cyclic compounds, the number of chlorine atoms possible in the molecule of rubber must be less by two for each isoprene group. Therefore, the chemical formula of the final product of chlorination of rubber by means of copper compounds must be $C_5H_6Cl_2$ and not $C_5H_6Cl_4$. The amount of chlorine in $C_5H_6Cl_2$ is 51.7%, which approaches very closely to our results.

The production of chemical derivatives of rubber ought to pass through the process of disaggregation, *i. e.*, a process of destruction of the elastic structure of rubber. This should be of economic advantage in manufacturing, and probably will have a favorable effect upon the quality of the resulting products.

Incidentally, it is necessary to mention the fact that only disaggregated rubber and not the oxidized rubber gives a good chlorinated product. To prove this, we introduced benzoyl peroxide (10% on the rubber) into the solution of rubber, and subjected the solution to 8 hours of ultra-violet radiation until the structure of the solution was destroyed. Following this, we chlorinated for one hour the rubber which had been destroyed in this manner. The product of chlorination contained 40.2% chlorine and was very unstable toward light and toward heat, and had a dark color. Evidently, benzoyl peroxide had only partially oxidized the rubber, and therefore after chlorination a product of poor quality was formed. In our future work, we shall investigate the production of other derivatives of rubber, using the basic theory which has been elaborated in this article.

Conclusions

1. Methods of production of chemical derivatives of rubber must be based upon the use of old, disaggregated raw material. The application of this principle to the production of chlorinated rubber has been firmly established, and thus offers the possibility, upon the basis of our first experiments, of developing methods for the production of chlorinated rubber.

2. The investigation of the process of chlorination of rubber disaggregated by means of copper compounds completely supports the authors' point of view concerning the character of the action of copper compounds on the rubber. The authors view this action as a disaggregation of the rubber, which destroys its elastic structure and transforms the rubber compounds into forms which are chemically reactive.

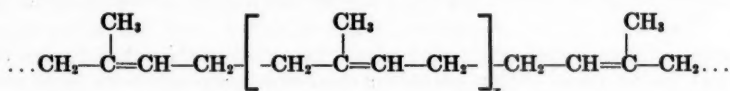
3. The process of chlorination of disaggregated rubber by means of copper compounds proves the authors' hypothesis about the mechanism of this disaggregation, which leads to the formation of cyclic compounds of rubber.

The Constitution of Rubber and the Nature of Its Viscous Solutions

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The Different Conceptions of the Constitution of Rubber.—It has been established by former research that rubber is a polymeric isoprene. The nature of the combination of the isoprene molecules in rubber was explained by Harries. From this work it follows that rubber is an unsaturated hydrocarbon of the formula:



but the molecular weight of rubber was unknown, as x , the magnitude of polymerization, was unknown. The outstanding question which arose was how the striking properties of rubber and the formation of colloidal solutions depended on the constitution and magnitude of the rubber molecule. This question has been answered in the last decade in two different manners. One set of workers (see particularly R. Pummerer, *Ber.*, **60**, 2167 (1927); Meyer and Mark, *Ber.*, **61**, 1939 (1928)) who paid special attention to colloidal properties, thought that the colloidal particles of rubber possessed a micellar structure. They were led to this conception by comparison with soaps, as there are many parallels in the behavior of soap solutions and those of rubber. Both solutions have high viscosities and do not obey the Hagen-Poiseuille law. Further, the viscosity of both colloidal solutions is very easily altered. These micellar ideas found support in the work of Pummerer (*Ber.*, **60**, 2167 (1927)) according to whom the formula of rubber should be $(\text{C}_5\text{H}_8)_n$. Just as the soap micelle is built up of small simple molecules, so the rubber micelle was considered to be built up by the combination of small simple $(\text{C}_5\text{H}_8)_n$ molecules. Pummerer appeared to be able to support his view with a great number of observations. The molecular weight of rubber and of hydorrubber (Pummerer and Koch, *Ann.*, **438**, 308 (1924)) in camphor appeared to agree with an eight-fold polymerized compound. It is noteworthy that isorubber nitrone, prepared from rubber and nitrosobenzene, gives solutions of low viscosity in which molecules of eight-fold polymerization are dissolved (Pummerer and Gündel, *Ber.*, **59**, 1591 (1928)).

In contradiction to these ideas is the knowledge, gained by examination of synthetic polymers (Staudinger, *Ber.*, **59**, 3019 (1926)), that rubber has very large molecules and that the important properties of rubber, both its elasticity (*Ber.*, **63**, 921 (1930)) and the high viscosity of its solutions, depend on the magnitude and configuration of its molecules. These latter conceptions were established by numerous experiments on rubber and balata, and also by control experiments on synthetic polystyroles (Staudinger and Heuer, "Die hochmolekularen organischen Verbindungen: Kautschuk und Cellulose," p. 157).

To conclude, therefore, from the similar behavior of the colloidal solutions of soap and rubber that their colloidal particles have a similar constitution (Meyer

and Mark, *loc. cit.*) is not correct. The constitution of the colloidal particles is fundamentally different. In the soap solution elongated micelles occur, but in rubber solution, on the other hand, very long thread-like molecules. The colloidal particles have in common only their extended configuration. This causes, in consequence of the great sphere of action of the extended particles, the high viscosity and also the abnormal flow of the solutions (Staudinger, *Ber.*, **63**, 921 (1930); *Kautschuk*, **1930**, 153; Staudinger, "Die hochmolekularen organischen Verbindungen: Kautschuk und Cellulose," p. 93). The variations of viscosity depend in the two cases on different causes. In the soaps these variations are to be ascribed to the fact that the micelles are extraordinarily labile bodies (Staudinger and Leupold, *Ber.*, **63**, 730 (1930)); for example, their magnitude is easily altered by variations of temperature. Further, the formation of micelles is strongly influenced by the hydrogen-ion concentration of the solution, and this may be noted in the variations of viscosity. The variations of viscosity of a rubber solution are, on the contrary, to be attributed to the great affinity for oxygen of very reactive molecules. They are readily decomposed by autoxidation, and this is accompanied by a marked irreversible diminution of the viscosity of the solution. In consequence of the reactivity of the molecules a marked decomposition occurs on melting rubber in camphor (Staudinger and Schaal, *Helv. Chim. Acta*, **13**, 1355 (1930)) and also under the influence of nitrosobenzene (Staudinger and Joseph, *Ber.*, **13**, 2888 (1930)). Therefore, Pummerer came to a mistaken conclusion in his determination of the molecular weight.

The correct determination of the molecular weight of rubber was obtained by measurements of the viscosity of its dilute solutions. From the law of viscosity (Staudinger, *Ber.*, **65**, 267 (1932); "Die hochmolekularen organischen Verbindungen: Kautschuk und Cellulose, p. 56) follows a simple method for determining the length of chain and therefore the molecular magnitude of compounds with thread-like molecules.

Viscosity Experiments on Low Molecular and Semi-Colloidal Polypranes and Polyphenes.—Between the viscosity of a dilute solution and the length of the chain of a compound with thread-like molecules there exists the following simple relation:

$$\eta_{sp(1.4\%)} = \gamma n$$

in which n is the number of members in the thread molecule. It is immaterial whether the members of the chain consist of carbon atoms or of carbon and oxygen atoms. $\eta_{sp(1.4\%)}$ is the specific viscosity in the 1.4 per cent solution, *i. e.*, the increase in viscosity produced by a solute in 1.4 per cent solution. γ is a constant, representing the viscosity increase due to one chain atom, and in a 1.4 per cent benzene solution is 1.3×10^{-3} . If the number of chain-forming atoms be n as calculated from a viscosity determination according to the above formula, then the molecular weights of both homologous and polymer-homologous compounds may be calculated. This molecular weight is equal to the product of the number of chain members, n , and the chain equivalent weight. The latter is defined as the average weight per chain carbon atom, obtained by dividing the total weight of the fundamental molecule by the number of chain atoms; it is therefore equal to the weight of the fundamental molecule divided by the number of chain-forming atoms. The validity of this law of viscosity was confirmed not only in the case of polymeric compounds, which are always mixtures of polymer-homologues, but also in the cases of simple substances with thread-like molecules, such as paraffins and paraffin derivatives (Staudinger and Nodzu, *Ber.*, **63**, 721 (1930); Staudinger and Ochiai, *Z. phys. Chem.*, **158A**, 35 (1931)).

According to this law of viscosity, the viscosity of the solution is largely independent of the composition of the dissolved compound with thread-like molecules. It depends solely on the length and number of the dissolved molecules. Therefore, both saturated and unsaturated compounds have equal viscosities at equal solution concentration, if the length of their molecules is the same. This fact was first established with semi-colloidal rubber and hydorrubber and then with balata and hydrobalata. In these cases, the molecular weight obtained by the cryoscopic method agreed with that calculated from the viscosity measurements (Staudinger and Nodzu, *Helv. Chim. Acta*, **13**, 1350 (1930)).

This result was contrary to the earlier views on the state of solution of substances of high molecular weight. It was thought that the high viscosity must be attributed to a strong solvation of the dissolved molecules, but, according to this, the solvation must be different in the cases of saturated and unsaturated molecules, and this is not the case, as the viscosity measurements show (Fikentscher and Mark, *Kolloid-Z.*, **49**, 135 (1929)).

The hemicolloidal polypranes and polyprenes are not simple substances, but consist of a mixture of polymeric homologues. The law of viscosity was, therefore, tested in the case of the uniform hydrocarbons squalene (Professor Heilbronn, Liverpool, kindly placed this hydrocarbon at the author's disposal), perhydrosqualene, and dibixan (the author has to thank Professor Karren, Zurich, for this hydrocarbon), that is to say, hydrocarbons which are closely related to the polypranes and polyprenes (Staudinger and Leupold, *Helv. Chim. Acta*, **15**, 221 (1932)). It was found that the law of viscosity was supported in every case. It is worthy of notice that squalene and perhydrosqualene show no difference in viscosity. It is therefore established that, in the case of simple compounds, the double linkages of the molecule exert no influence on the specific viscosities of their solutions.

TABLE I

Substance	Formula	Number of Chain Carbon Atoms	η_{sp} (1.40%) Calculated = $1.3 \times 10^{-3} \times n$	η_{sp} (1.4%) by Experiment
Squalene	$C_{30}H_{50}$	24	0.031	0.032
Perhydrosqualene	$C_{30}H_{62}$	24	0.031	0.032
Dibixan	$C_{46}H_{94}$	38	0.049	0.055

According to the law of viscosity, the viscosity of different substances in solutions of equal concentration depends only on the number of chain members of the molecule, and is independent of the number and magnitude of the side-chains of the molecules. In different substances with thread-like molecules of equal length, some having side-chains and others not, the individual fundamental molecules have different weights; it follows that the numbers of molecules in 1.4 per cent solutions are different. The viscosity of the solutions is, however, independent of whether many "thin" or few "thick" molecules of equal length are dissolved, it is the same with equal concentration. A new proof of the conformity to this law may be advanced by examination of solutions of squalene hexahydrochloride and squalene hexahydrobromide. The viscosity of these halogen substitution products of squalene in equal concentration is the same as that of squalene and of perhydrosqualene, though in a solution of squalene hexahydrobromide, there are only half as many molecules as in a squalene solution of equal concentration (unpublished work of E. O. Leupold).

These values which agree with the law provide a further proof that the molecules in solution possess the same rigid rod shape as in the solid state. Of course, these molecules vibrate in solution, and the vibrations must be regarded as elastic ones;

however, in their mean position, the molecules possess rod shape. If the molecules in solution were bent or interwoven, then in the different squalene derivatives these bendings and entanglements of the molecules would be quite different, and it would not be anticipated that simple relations should obtain between viscosity and length of chain (Kuhn, *Z. phys. Chem.*, **A161**, 1 (1932); R. Signer, *Z. phys. Chem.*, **A165**, 183 (1933)).

Determinations of the Molecular Weights of Rubber and Balata.—The validity of the law of viscosity has been proved by the experiments already described, as also by a number of other workers in the case of high polymers in substances of molecular weight from 8000 to 10,000; such substances must have a degree of polym-

TABLE II
 η (SP/4%) OF SQUALENE AND ITS DERIVATIONS DISSOLVED IN CS_2 AND CCl_4

Substance	CS_2	CCl_4
Squalene	0.036	0.041
Perhydrosqualene	0.036	0.039
Squalene hexahydrochloride	0.036	0.044
Squalene hexahydrobromide	0.029	0.038

erization of from 10 to 150, and therefore possess a number of chain atoms up to 600 atoms. Hence by means of viscosity measurements the lengths of chain may be determined, *i. e.*, the molecular weights of still much longer molecules. According to Kraemer and van Natta (*J. phys. Chem.*, **36**, 3175 (1932)), the law of viscosity is not suitable for the evaluation of the molecular weight of rubber (*cf.* Staudinger, *Ber.*, **67**, 92 (1934)); but the sphere of validity of the law of viscosity has been extended in other cases, *e. g.*, to cellulose derivatives of length 1200 A.U. (Staudinger, "Die hochmolekularen organischen Verbindungen: Kautschuk und Cellulose," p. 465).

In order to determine the molecular weights of rubber and balata, very dilute solutions must be used. Such solutions should have a specific viscosity of not more than 0.3 at most. In solutions of higher viscosity, such as were formerly examined as a rule, the law of viscosity did not apply. Measurements of this kind are, therefore, useless for the determination of molecular weights. Again, attention must be given to the fact that rubber solutions are affected by atmospheric oxygen, especially if exposed to light. Therefore, the viscosity determinations must be carried out in solvents carefully freed from air (Staudinger and Leupold, "Die hochmolekularen organischen Verbindungen: Kautschuk und Cellulose," p. 438). As a result of such measurements for different sorts of rubber and for balata, the values (Table III) for molecular weights and dimensions of the molecules are obtained.

It should be noted that solutions of hemicolloidal and eucolloidal polyprenes do not exhibit precisely the same behavior as rubber solutions, for solutions of eucolloidal rubber do not obey the Hagen-Poiseuille law. In these solutions the long rod-shaped molecules are turned in the direction of the current, and the greater the velocity of flow, the greater this tendency. In consequence of this orientation of the molecules the viscosity is lower than if the molecules were irregularly distributed, as is the case with solutions of hemicolloids. In the case of eucolloids, therefore, the viscosity is not proportional to the length of the molecules but is rather smaller than that required by the true length of the molecules. Therefore the true molecular weights of eucolloidal rubbers are still greater than the values given above. As, however, in very dilute solutions the variations from the Hagen-Poiseuille law are negligible, the errors in the determination of the

molecular weight of rubber are similarly negligible in determinations which are carried out in solutions of very low viscosity.

TABLE III

Substance	η_{sp} (1.4%) by Experiment	Degree of Polymeriza- tion = $\frac{\eta_{sp} (1.4\%)}{4 \times 1.3 \times 10^{-3}}$	Molecular Weight	Number of Chain Carbon Atoms	Length of Molecule in A.U.
Purified rubber, soluble in benzene	6.72	1300	88000	5200	5800
Purified rubber, soluble in ether	4.86	930	64000	3700	4200
Masticated rubber	1.57	300	20000	1200	1350
Balata	3.09	590	40000	2400	2650
Disintegrated balata	0.52	100	6800	400	450

The molecular weights of rubber and balata, and even of masticated rubber agree in order of magnitude with the particle size deduced from osmosis (Caspari, *J. Chem. Soc.*, **105**, 2139 (1914); Meyer and Mark, *Ber.*, **61**, 19,139 (1928); Kroepelein and Bumshagen, *Ber.*, **61**, 2441 (1928); Wo. Ostwald, *Kolloid Z.*, **49**, 60 (1929); the assertions of Schultz, *Z. phys. Chem.*, **161**, 441 (1932), that the molecular weights of rubber from osmotic and viscosity determinations do not agree, are based on an erroneous calculation. It is now established, as will again be pointed out in what follows, that isolated single molecules occur in a dilute rubber solution. So, by the osmotic experiments, the micelle weight of rubber is not determined, as was formerly thought, but the true molecular weight of rubber. The determinations of the earlier workers certainly could not give precise values, for sufficient attention had not been given to the extraordinary sensitiveness of rubber, for instance, to oxygen dissolved in the solvent. Therefore, such osmotic measurements should be repeated with complete exclusion of oxygen.

Evidence for the Molecular Constitution of the Colloidal Particles of Rubber and of Balata.—The determination of the molecular weight of rubber described in the last section is dependent on the assumption that in a dilute solution rod-shaped molecules really occur, and that the particles are not micelles as was formerly thought. The proof of the identity of the colloidal particles with the macromolecules was established in earlier work by chemical processes. A polymeric homologous series of polyprenes was prepared. By means of these, it was possible to show that the physical properties of the products varied regularly with increasing molecular weight. So it could be proved that the characteristic properties, of rubber are chiefly a function of the length of its molecule. The molecular constitution of its colloidal particles could further be elucidated by viscosity tests. Therefore, these not only provide information of the magnitude of the particles, but also give knowledge of the composition of the colloidal particles. Solutions of particles of micellar composition, as for instance, soap solutions, show entirely different viscosity behavior under changes of temperature and concentration from a solution with molecules as colloidal particles (Staudinger and Leupold, "Die hochmolekularen organischen Verbindungen: Kautschuk und Cellulose," p. 404; Staudinger and Bondy, *Ann.*, **488**, 127 (1931)).

Further proofs of the identity of the colloidal particles of a rubber solution with the macromolecules may be conclusively advanced chemically, for by chemical reactions of the unsaturated rubber, derivatives must be obtained which have the same chain length as the original hydrocarbon, that is, of course, if no decomposition of the unstable molecule has occurred in the course of the reaction. This may be proved by viscosity tests, for, according to the law of viscosity, solutions

of equal concentration of substances with thread-like molecules have equal viscosity, independent of the special constitution of the molecules.

To decide this question, the hydrogenation of rubber and of balata was considered from the following points of view. (For earlier work on the hydrogenation of rubber and of balata, see *Helv. Chim. Acta*, **5**, 785 (1922); *Ber.*, **57**, 1203 (1924); *Helv. Chim. Acta*, **7**, 842 (1924); **13**, 1324, 1334, 1375 (1930).) If the colloidal particles really are long unsaturated macromolecules, then it must be possible, by careful reduction, to produce the polymeric analogues hydrorubber and hydro-balata, that is, products with equal numbers of chain carbon atoms with the unhydrogenated products. Polymeric-analogous products are substances of equal degree of polymerization, and therefore of equal chain length, but they differ in the kind of side chain or in the special constitution of the molecule; for example, squalene and perhydrosqualene are polymeric analogues. These polymeric analogous hydrogenation products should then, in solutions of equal concentration, display the same viscosities as the original products. This is really the case as the following table shows (Staudinger and Leupold, *Ber.*, **67**, 304 (1934)).

TABLE IV
VISCOSITY MEASUREMENTS OF POLYPRENES AND OF POLYMERIC ANALOGOUS POLYPRENES

Substance	Concentration, Per Cent	η_{sp} by Experiment	η_{sp} (1.4%)	Number of Chain Members $n = \frac{\eta_{sp} (1.4\%)}{1.3 \times 10^{-3}}$	Molecular Weight $= n \times \text{Equivalent}$
Semi-colloidal balata	0.85	0.315	0.52	400	6800
Semi-colloidal hydrobalata, reduced to 100 per cent	0.68	0.217	0.45	345	6000
Balata	0.34	0.75	3.09	2400	40000
Hydrobalata (100 per cent reduction)	0.35	0.767	3.07	2360	41000
Rubber, Fraction I	0.136	0.472	4.86	3700	64000
Hydrorubber, Fraction I (reduced to about 50 per cent (a))	0.125	0.418	4.68	3600	63000
Hydrorubber, Fraction I (reduced to about 100 per cent (b))	0.118	0.431	5.12	3900	69000
Rubber, Fraction II	0.136	0.610	6.28	4800	82000
Hydrorubber, Fraction II (reduced to about 50 per cent (a))	0.148	0.650	6.15	4700	82000
Hydrorubber, Fraction II (reduced to about 50 per cent (b))	0.18	0.760	5.92	4550	80000
Rubber, Fraction III	0.136	0.653	6.72	5200	88000
Hydrorubber, Fraction III (reduced to almost 100 per cent)	0.088	0.362	5.76	4450	78000

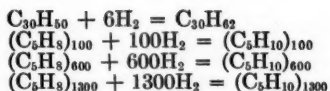
Equivalent = Chain equivalent weight

$$= \frac{\text{Fundamental molecular weight}}{\text{Number of chain atoms}} = \frac{68}{4} = 17 \text{ for rubber}$$

$$= \frac{70}{4} = 17.5 \text{ for hydrorubber}$$

These chemical transformations show that, in a solution of rubber and balata, macromolecules exist and no colloidal particles of micellar construction. Reactions may be carried out with these macromolecules in the same way as with molecules of substances of lower molecular weight without altering their magnitude. The reduction of rubber to hydrorubber is comparable with the transformation of squalene into hydrosqualene, and may be expressed in the following formulas:

Squalene
Hemicolloidal balata
Balata
Rubber



Therefore in the polyprenes of high and low molecular weights in rubber, just as in squalene, compounds with molecules built up on the same principle are present and they differ only in magnitude.

The Preparation of Hydrorubber.—The conversion of rubber into hydrorubber of the same molecular magnitude is exceedingly difficult to accomplish, and requires wide experience of the instability of rubber. The earlier reductions of rubber were carried out at a rather high temperature with platinum as a catalyst, in 1922 (Staudinger and Fritsch, *Helv. Chim. Acta*, 5, 785 (1922)). At the same time Pummerer and Burkard, (*Ber.*, 55, 3458 (1922)) undertook the reduction of rubber in dilute solution. Apparently they did not at first obtain any hydrorubber, for they described its properties, regarding it as an auto-oxidizable substance (cf. Staudinger, *Ber.*, 57, 1207 (1924)). These experiments produced semi-colloidal hydrorubber (Staudinger, *Helv. Chim. Acta*, 13, 1324 (1930)). If, on the other hand, rubber be reduced in dilute solution, then hydrorubber of higher molecular weight may be obtained, but at the same time the molecule of the rubber is decomposed, and this is done by the oxygen present in the solvent (Staudinger and Feiszt, *Helv. Chim. Acta*, 13, 1361 (1930)). In order then to produce eucolloidal hydrorubber of high molecular weight, the molecules of which have the same length as those of rubber, the reduction must be carried out with extraordinary care, so that neither cracking nor splitting of the molecules is caused by atmospheric oxygen. This reduction, therefore, must be carried out in very dilute solution, with scrupulous exclusion of oxygen, with solvents free from air and with a highly active nickel catalyst, at a temperature of 100° to not above 120°, at most. The reduction must be carried out in a rotating autoclave under a pressure of 100 atmospheres of hydrogen. Under these conditions it is possible to prepare eucolloidal hydrorubber and hydrobalata of high molecular weight (These experiments were performed by Leupold, cf. Staudinger, "Die hochmolekularen organischen Verbindungen: Kautschuk und Cellulose," p. 404, also *Ber.*, 67, 304 (1934).)

The Physical Properties of Polyprenes and Polyprenes.—The preparation of eucolloidal hydrorubber is of great importance, for from it a further proof is advanced that the physical properties of solid rubber as well as those of a rubber solution are entirely a function of the chain length, for a solution of hydrorubber shows the same viscosity behavior as a solution of a polymeric-analogous rubber. There is no difference in the appearance of solid rubber and solid hydrorubber. Thus an answer is offered to the frequently discussed question, whether and to what degree the elasticity of rubber is connected with its unsaturated nature (cf. Kirchhoff, *Kolloid.-Z.*, 30, 176 (1922); Meyer and Mark, *Ber.*, 61, 1944 (1928); Fikentscher and Mark, *Kautschuk*, 1930, 2; Kirchhoff, *Kautschuk*, 1930, 31). It was formerly thought, apparently with support from observations, that hydrorubber, contrary to rubber, was not elastic (Staudinger and Fritsch, *Helv. Chim. Acta*, 5, 789 (1922)). The hydrorubber formerly prepared in the form of a more or less syrupy mass was, however, a hemicolloid. The change in elastic properties caused by the conversion from rubber into this hemicolloidal hydrorubber is not to be attributed to the reduction but to the diminution in molecules due to the reduction at higher temperature. Hemicolloids do not generally display the elasticity characteristic only of eucolloids. That the elasticity of rubber is not

due to the double linkages in the molecule, but is essentially only connected with the macromolecular constitution of the body, is definitely proved by the fact that macromolecular perhydropolymer possesses elastic properties similar to those of rubber itself (Staudinger, "Die hochmolekularen organischen Verbindungen: Kautschuk und Cellulose," p. 122; Staudinger and Machemer, *Ber.*, **62**, 929 (1930); Meyer, Susich, and Valko, *Kolloid-Z.*, **59**, 212 (1932), have expressed substantial agreement with the views in the papers quoted. Cf. Staudinger, *ibid.*, **60**, 296 (1932).).

Elasticity is a property common to many substances of high molecular weight; it is also confined to a definite temperature. Thus, substances which are not elastic at ordinary temperature, such as polystyrol, become elastic on warming (Staudinger, *Ber.*, **59**, 3036 (1926)). The closer relationships between elasticity and the constitution of the molecules are not yet known (cf. the statements of Sauter, *Z. phys. Chem.*, **21B**, 181 (1932)).

The Colloidal Nature of Rubber.—The most striking property of a rubber solution is its viscosity, which may be exceedingly high in solutions of low concentration. Two per cent to 3 per cent solutions of rubber have an η_r value of about 100, that is, they are a hundred times as viscous as the solvent, but a 2 per cent to 3 per cent solution of a terpene of lower molecular weight in benzene has almost the same viscosity as the solvent. What is the cause of this phenomenon, that the long thread-like molecules of rubber produce such an abnormal viscosity when in solution?

The explanation is a very simple one. According to Einstein's Law:

$$\eta_r = 1 + K\Phi \text{ or } \eta_{sp} = K\Phi \quad (1)$$

In solutions of equal concentration then, the viscosity should be independent of the degree of dispersion:

$$\frac{\eta_{sp}}{c} = K \quad (2)$$

The validity of these relationships has also been proved for some suspensions, such as mastic suspension, by Blancelin (*Compt. rend.*, **152**, 1382 (1911)). In the same way the viscosity of a standard molar solution of molecular colloids should be the same, no matter whether many small or few large molecules are dissolved:

$$\Phi = \zeta_1 n_1 = \zeta_2 n_2 = \zeta_3 n_3 = \dots \quad (3)$$

when ζ stands for the volume of a particle, and n for the number of particles. As the number of particles decreases with increasing molecular weight (M), the following relation should exist:

$$\Phi = \frac{\zeta_1}{M_1} = \frac{\zeta_2}{M_2} = \frac{\zeta_3}{M_3} = \dots \quad (4)$$

In the case of spherical molecules, the specific viscosity of solutions of equal concentration is actually almost independent of the magnitude of the molecules (Staudinger and Heuer, *Ber.*, **63**, 226 (1930)). In the case of thread-like molecules of a polymeric homologous series, on the other hand, the viscosity of solutions of equal concentration increases proportionally to the length of chain, so the following relationship holds:

$$\frac{\eta_{sp}}{c} = K_m \cdot M \quad (5)$$

Therefore, here, the total volume of the dissolved phase, Φ , is not constant, but increases in proportion to the molecular weight, that is, to the length of chain:

$$\frac{\Phi_1}{\Phi_2} = \frac{M_1}{M_2} \text{ or } \frac{\Phi_1}{M_1} = \frac{\Phi_2}{M_2} \quad (6)$$

It follows that the volume of the dissolved particles does not vary as the molecular weights, but as the squares of the molecular weights, for, as $\Phi = \frac{\xi}{M}$, so from (6):

$$\frac{\xi_1}{M_1^2} = \frac{\xi_2}{M_2^2} = \frac{\xi_3}{M_3^2} = \dots \quad (7)$$

To understand this relation, one may imagine that a long thread-like molecule, when it is in solution, occupies by reason of its vibrations, a greater volume than its own. (Staudinger, *Ber.*, 63, 921 (1930); *Kolloid-Z.*, 51, 71 (1930); *Z. phys. Chem.*, 153A, 391 (1931).) The spheres of activity of the thread-like molecules vary as the square of the chain lengths, and therefore as the square of the molecular weights. A solution of a polyprene of low molecular weight, and therefore, of a decomposed rubber contains many small molecules with restricted spheres of activity. As the number of molecules decreases only proportionally to the chain length the sphere of activity increases proportionally to the square of the chain length. In the case of substances of high molecular weight, such as rubber, composed of long thread-like molecules, a condition is soon attained where the total sphere of activity of the molecules is greater than the volume of solution at their disposal. In other words, the molecules no longer have space enough for free movement in the volume of solution. They mutually obstruct one another, and this produces the high viscosity of the solution.

A very dilute solution in which the long molecules have freedom of movement should be called a sol solution. In such a solution the thread-like molecules are in the same normal condition of solution as any substance of low molecular weight in dilute solution. The condition of solution in which the long molecules mutually obstruct one another is a new sort of condition, which does not occur in the case of substances of low molecular weight. A solution in which the total sphere of activity of the long molecules is greater than the volume of the solution is called a gel solution. From gel solutions there is a continuous transition to gels, in which the mobility of the long molecules is completely restricted. Such a gel condition cannot be obtained with substances of low molecular weight, for the molecules extend almost equally in all dimensions, and, therefore, the sphere of activity of a molecule is almost identical with its own volume.

TABLE V

	Average Molecular Weight	Degree of Polymerization	No. of Molecules in 1 Cc. 0.1 Fundamental Molar Solution†	Sphere of Activity in A.U.		Per Cent of Total Volume	Limiting Concentration	
				Of a Thread-like Molecule*	Of All Molecules in 1 cc. Fundamental Molar Solution		In Fundamental Molarity	Per Cent
Pure rubber	68000	1000	6×10^{16}	4×10^7	$2 \times 4 \cdot 10^{24}$	240	0.041	0.28
Hemicolloidal rubber	6800	100	6×10^{17}	4×10^8	$2 \times 4 \cdot 10^{23}$	24	0.41	2.8
Polyprene of lower molecular weight	680	10	6×10^{18}	4×10^9	$2 \times 4 \cdot 10^{22}$	2.4	4.1	28

† A fundamental molar solution is one containing 1 gram-molecule of C_5H_8 per liter.

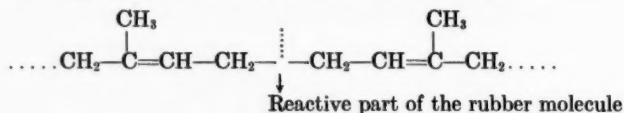
* Length of isoprene residue = 4.2 A.U.; diameter, 3 A.U.

The concentration at which a sol solution is converted into a gel solution has been called its limiting concentration (cf. *Ber.*, **63**, 930 (1930)). As Table V shows, in the case of rubber of very high molecular weight, a sol solution is obtained only in extremely low concentration (less than 0.28 per cent). The highly viscous 1.6 to 2 per cent solutions are gel solutions in which the molecules no longer have unrestricted mobility. Solutions containing less than 28 per cent polyprene with degree of polymerization 10 are sol solutions.

The deviations from the Hagen-Poiseuille law noted in the flow of rubber solutions (Wo. Ostwald, *Kolloid Z.*, **36**, **99**, 157, 248 (1925)), which formerly gave rise to comparison with soap solutions, are easily explained. These abnormal behaviors of flow are dependent on the shape and length of the molecules (Staudinger and Bondy, *Ann.*, **488**, 134 (1931)). The abnormalities become greater the higher the molecular weight of the rubber and the more concentrated the solutions. The more rapidly a solution flows, if it contains long molecules, the more the molecules become parallel to one another (Signer, *Z. phys. Chem.*, **150A**, 257 (1930)). The mutual disturbances of the particles are diminished by their orientation, and in consequence there is a diminution of viscosity. As deviations from the Hagen-Poiseuille law in these substances depend on the length of the molecules, therefore, they are called macromolecular viscosity phenomena (Staudinger and Machemer, *Ber.*, **62**, 2921 (1929)). With hemicolloids they do not occur; disintegrated rubbers therefore display normal behavior of flow. As masticated rubber is highly disintegrated, its solutions obey the Hagen-Poiseuille law. (Formerly it was considered, to explain these observations, that a rubber solution had a definite structure which was destroyed by mastication.)

Again, the differences in swelling phenomena shown by rubbers of high molecular weight and by those of low molecular weight, are explained by this new knowledge of the constitution of rubber (Staudinger, *Kolloid Z.*, **54**, 135 (1931)). The large molecules, because of their wide sphere of activity, are so slowly dissolved out of the solid substance that the solvent can press in between them before they are dissolved, and this causes swelling. For this reason, the swelling phenomena in the case of undegraded rubbers of high molecular weight are much more marked than in the case of degraded masticated rubber.

Chemical Properties of Rubber.—Rubber is an unsaturated hydrocarbon which can take up hydrogen, halogen, or halogen chloride at the double linkage and is especially sensitive to oxygen. The reactive positions are the ethylene linkings. Again, because of the particular position of the double linkage as an "allyl grouping," the single linkage between the carbon atoms is very labile:

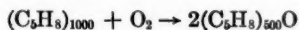


That is the reason why rubber may be so easily "cracked," and why saturated hydorrubber is much more stable. (Staudinger and Rheiner, *Helv. Chim. Acta*, **7**, 25 (1924); Staudinger, *Ber.*, **57**, 1203 (1924); Schmidt, *Z. phys. Chem.*, **A159**, 337 (1933).

The thread-like molecules of the polyprenes are increasingly unstable with increasing length. Therefore, a rubber of higher molecular weight cracks more readily than one of lower molecular weight. The great instabilities of long molecules may be compared with the great fragility of long, thin rods.

The great sensitivity of rubber to oxygen is of particular note. It is not yet

determined whether the oxygen attaches itself at the double linkage or at the allyl group. If it is supposed that oxygen decomposes rubber according to the following general scheme:



it is clear that an exceedingly small mass of oxygen is needed to make a great change in the physical properties of rubber, for rubber, with molecules decomposed into one-half the length of the original, exhibits different physical properties. 3.3 cu. mm. of oxygen or 0.012 cc. of air suffice to decompose the rubber in 10 cc. of a 0.1 per cent rubber solution according to the equation given above. The specific viscosity of this solution drops from about 0.4 to 0.2, that is by 50 per cent. These small masses of air are often contained in the solvent and they cause an alteration in the rubber. Therefore, as stated above, measurements of rubber solutions must be carried out with most scrupulous exclusion of oxygen. (Staudinger and Leupold, *Ber.*, **63**, 730 (1930).)

Soluble and Insoluble Rubber.—The action of oxygen on rubber causes the above decomposition of the molecules in solution. On the other hand, in the solid state, oxygen can so act that the thread-like molecules of rubber are joined together in several places by bridges of oxygen. (Cf. Staudinger and Bondy, *Ann.*, **488**, 153 (1933); Staudinger and Leupold, "Die hochmolekularen organischen Verbindungen: Kautschuk und Cellulose," p. 442.) Because of this, soluble β -rubber of unlimited swelling capacity is converted into soluble rubber of limited swelling capacity. In the latter the long thread-like molecules are still solvated by the molecules of the solvent, which arrange themselves in a monomolecular layer round the thread-like molecules, but the single thread-like molecules can no longer be separated from one another, because of the oxygen bridges. Such union of the thread-like molecules may also be caused by the action of light, with linkage of carbon atoms. If these disturbing influences be excluded so that rubber be kept free from oxygen and light, then, even on long standing, there is no transformation of soluble into insoluble rubber. Therefore, the conversion of soluble into insoluble rubber is not, as was formerly thought, a colloid chemical action, but a chemical action. In the course of this action three-dimensional macromolecules are produced from thread-like molecules.

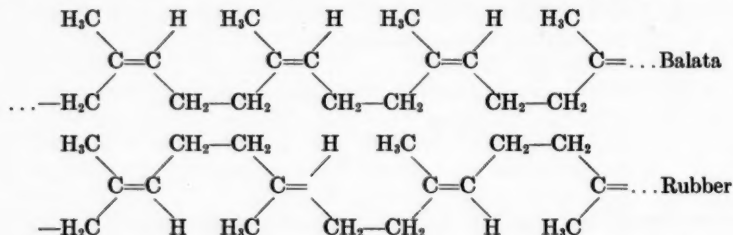
Contrary to former views (Bary and Hauser, *Kautschuk*, **1928**, 97) this insoluble rubber cannot be converted into the soluble variety by a reversible reaction. The soluble rubber prepared from this insoluble variety, by mastication or by powerful action of oxygen, is a vastly decomposed product. It is obtained from the insoluble rubber by destroying the three-dimensional macromolecules either by the action of oxygen or by mechanical tearing.

The Mastication of Rubber.—Masticated rubber, when dissolved, gives less viscous solutions than does unmasticated rubber. Formerly it was thought that the micellar structure of the rubber was altered during mastication (cf. for instance, Harries, *Ber.*, **56**, 1050 (1923); Ostwald, "Welt der vernachlässigten Dimensionen," **1927**, 10th Ed., p. 263). As a matter of fact, rubber is chiefly decomposed during mastication by the action of oxygen, but the long thread-like molecules may also be mechanically torn (Staudinger, "Die hochmolekularen organischen Verbindungen: Kautschuk und Cellulose," p. 379; Busse, *Ind. Eng. Chem.*, **24**, 140 (1932)).

Synthetic Rubber.—When once the constitution of rubber has been explained, it is clear that no synthetic rubbers obtained by the polymerization of isoprene can completely resemble natural rubber. The chain reaction (Staudinger, "Die hochmolekularen organischen Verbindungen: Kautschuk und Cellulose" p. 149) by

which the preparation of highly polymerized molecules is brought about, is early interrupted in the presence of catalysts. Therefore, the synthetic rubbers have not such high molecular weights as the natural rubbers. Also, during the synthesis, lateral linking between the single thread-like molecules may occur, and therefore the synthetic rubber is very frequently insoluble and possesses only limited swelling properties.

Rubber and Balata.—Gutta-percha and balata are identical. Rubber and balata are stereoisomeric (Staudinger, *Ber.*, **63**, 927 (1930); *Kautschuk*, **5**, 129 (1929)). In the case of substances of lower molecular weight, the modification with the higher melting point is regarded as the *trans* form, that with the lower melting point as the *cis* form. It may be, in the case of the hydrocarbons of high molecular weight that this is reversed, for the *cis* form possesses a more symmetrical molecule than the *trans* form, as is shown in the formulas below. The hydrocarbon with the symmetrical molecule will crystallize better and have a higher melting point than that with the unsymmetrical molecule. Therefore balata, which crystallizes well, will be in the *cis* form, in spite of its higher melting point.



Latex.—Latex is an approximately 30 per cent suspension or emulsion of almost spherical rubber particles in an albumen solution. The viscosity of an approximately 1 per cent latex is hardly higher than that of water. The relative viscosity is 1.05, but a 1 per cent solution of rubber in benzene is 30 to 50 times as viscous as the solvent. Therefore, a latex particle contains about 10^7 macromolecules of rubber. This comparison of latex, a suspension, with the solution of rubber in benzene, shows that the shape and not the magnitude of the particles determines the viscosity of a solution. As spherical particles have a sphere of activity almost identical with their own volume, solutions with such particles can never have a high viscosity. The high viscosity of rubber solutions, as has been pointed out, depends on the wide sphere of activity and the mutual interference of the long thread-like molecules.

A highly concentrated latex, such as "Revertex," dissolves in water without swelling, because of the spherical shape of the particles; whereas rubber swells strongly in organic solvents.

Molecular Colloids and Micellar Colloids.—Now that the constitution of rubber and the nature of its colloidal solutions has been explained, it will be understood why earlier workers clung to the mistaken idea of ascribing to the colloidal particles in a rubber solution the same constitution as that of the colloidal particles in a soap solution. Both have much in common. The micelles of a soap solution are elongated bodies (Theissen and others, *Z. phys. Chem.*, **156**, 435 (1931)), just like the rod-like molecules of a rubber solution. In consequence of the shape of the colloidal particles both solutions show high viscosity and abnormal behavior of flow, for, in a soap solution, too, the high viscosity is caused not by special solvation phenomena of the micelles, but particularly by their shape. The composition

of the colloidal particles is, however, entirely different (Staudinger, *Helv. Chim. Acta*, **15**, 221 (1932)). In a soap solution, the small fatty acid molecules are held together by intermolecular force. That is why the rod shaped micelles are very unstable, as is shown for instance, by the marked variation of viscosity when the soap solution is warmed. In a rubber solution, on the contrary, there are thread-like molecules in which the individual isoprene residues are joined together by their principal valencies to form a macromolecule. The instability of the rubber solution is determined by the unsaturated nature of the rubber molecule. These colloids, which were formerly described as lyophile colloids, therefore belong to entirely different groups. The one set are micellar colloids, the other set are molecular colloids.

By explanation of the constitution of rubber and other substances of high molecular weight, the nature of their viscous solutions was demonstrated. These new perceptions led finally to a new classification of the colloids (Staudinger, *Ber.*, **62**, 2893 (1929)).

The Mastication of Rubber

J. Behre

HAMBURG

Probably from the beginning of the rubber industry no process has changed so little as that for softening raw rubber, its so-called mastication. Although Hancock's machine, the masticator (1826), consisted of an internal rotating roll and a stationary shell, and modern machines have two rotating rolls, the same principle has always held true, *viz.*, a compression and consequent stretching of the rubber by means of great friction. Even enclosed mixers are essentially only a development of the Hancock principle, the value of which naturally will not be discussed here.

In spite of such long experience, the process of mastication is not clearly understood, and it is remarkable that there has apparently been little interest in this problem until recently. Only within the last few years has it received somewhat more attention, and attention should be called to the work of Cotton,¹ in which there is a compilation of the literature. As a result of this lack of knowledge, the conditions under which the most rational processes of mastication can be carried out have not been established, and even today the manufacturers of machines produce for the most part mills which have the most widely varying constants, without any satisfactory reasons for the particular constructions. The following discussion aims therefore to contribute toward the establishment of these conditions, and at the same time to view critically the various theories of the process of mastication. In this discussion plasticity values obtained by the method of Marzetti have been used as a measure of the degree of mastication since, as I have been able to show earlier² and has recently been confirmed by others,³ these plasticity values approach most nearly to practical conditions.

What Factors Influence This Degree of Mastication?

Apart from the personal views of the author, which are not susceptible of analysis without further investigation, Talalay⁴ gives ten factors, which may be grouped under three headings:

1. The load on the mill.
2. The constants of the rolls.
3. The temperature of the rolls.

In so far as the size of the load is concerned, it is obvious without further discussion that, with the smallest loads, each unit working surface of the roll must have the maximum effect, provided that time is chosen as a unit of measure, for with relatively small quantities every particle passes between the rolls more frequently than with larger quantities of rubber. Naturally the thickness of the layer of raw rubber also plays a part, and a few experiments were carried out to show this effect. The results are summarized in Table I and Fig. 1.

It is evident from these measurements that, with increase in the thickness of the layer of rubber, the effect of milling becomes less. However the optimum degree of mastication does not correspond, as would be expected, to the smallest thickness which was tested, *i. e.*, 4 millimeters, but to 6. This is explained by the fact that in these experiments the weight of raw rubber which the rolls carried was kept

constant, namely, 17.3 kg., a quantity which is just sufficient to cover the surface of the front roll with a layer 6 millimeters thick. With a thickness of 4 millimeters, the surface of the layer of rubber became too great with respect to the surface of the roll, so that every particle no longer passed between the rolls as frequently as at a thickness of 6 millimeters, and consequently the degree of mastication was less.

TABLE I

First Latex Crepe: 17.3 Kg.; Plasticity: 13; Temperature of the Front Roll: 50° C.

Time of Milling	Thickness of the Sample in Millimeters				
	4	6	8	10	12
2	20	18	13	15	15
4	35	37	37	26	26
6	48	51	51	41	35
8	50	59	68	49	45
10	58	73	71	60	60
15	71	89	83	69	69
20	90	96	90	75	80

At thicknesses of 8, 10, and 12 millimeters the rubber passed more often between the rolls, but unless it was cut continually only the outer layer was masticated, as was easily determined by a plasticity test. Therefore the plasticity of the total mass was less.

TABLE II
Mill Constants

No. of Roll	Length of Bank in M.	Dia-meter in M.	Area in Sq. M. of Rolls	Revolutions per Min.		Speed in M. per Min.		Fric-tional Ratio	Load in Kg.
				Front Roll	Back Roll	Front Roll	Back Roll		
1	0.550	0.380	0.655	8.180	12.180	9.771	14.540	1:1.50	4.3
2	0.800	0.400	1.000	10.260	14.760	12.900	18.550	1:1.44	6.7
3	1.000	0.400	1.257	10.390	15.510	13.060	19.500	1:1.49	8.4
4	1.200	0.500	1.884	10.700	15.500	16.800	24.350	1:1.45	12.5
5	1.500	0.550	2.594	11.250	16.875	19.463	29.194	1:1.50	17.3
6	1.000	0.400	1.257	11.880	18.000	14.930	22.620	1:1.52	8.4
7	1.100	0.450	1.555	12.787	19.512	18.030	27.520	1:1.52	10.4
8	1.200	0.500	1.884	13.548	19.512	21.270	30.630	1:1.44	12.5
9	1.500	0.500	2.356	13.771	19.000	21.621	29.830	1:1.38	15.6
10	1.000	0.400	1.257	14.516	20.830	18.290	26.250	1:1.43	8.4
11	0.800	0.410	1.030	15.868	21.640	20.440	27.870	1:1.36	6.9

TABLE III

First Latex Crepe; Plasticity: 20; Temperature of the Front Roll: 50° C.

No. of Mill	Kg.	Milling Time in Minutes						
		2	4	6	8	10	15	20
1	4.3	26	30	36	42	59	76	95
2	6.7	39	41	51	58	67	..	110
3	8.4	44	47	48	51	56	65	70
4	12.5	40	43	53	53	57	61	76
5	17.3	23	35	48	57	64	80	91
6	8.4	30	47	50	63	70	76	97
7	10.4	38	40	44	49	51	67	78
8	12.5	26	31	38	46	53	74	84
9	15.6	38	49	53	61	61	84	91
10	8.4	42	43	57	60	62	76	83
11	6.9	40	50	50	61	65	70	86

We thus come to the second factor, the mill constants, length of the bank, diameter, rate of rotation, and frictional ratio. Table II gives data on the mills which were used in the investigation, while Table III shows the plasticity values.

The load on the mills was so chosen that in every case the layer of rubber was 6 millimeters thick. Samples were removed after 2, 4, 6, 8, 10, 15, and 20 minutes. As represented graphically in Fig. 2, the plasticity values are shown in relation to the rate of rotation of the front roll. For the sake of clearness, the results of only the 6, 10, and 20 minute samples are given.

If the values for the 6 minute period are considered first of all, it will be seen that the degree of mastication increases as the circumferential speed of the front roll increases. (The values in the graph represent the numbers of the mills in Table II.) In a striking way the points lie on two straight lines which run parallel to one another, that is, 1, 2, 3, 6, 4, and 10 are on one line and 7, 5, 9, and 11 are on the other, while 8 lies wholly outside the series. If on the other hand the plasticity values are plotted against the rates of rotation, as is seen in Fig. 3, these differences disappear, and under these conditions the greater the rate of rotation the greater is the extent of mastication.

Only mills 8 and 11 fall completely outside the series. At higher degrees of mastication on the contrary, mills 1, 2, 5, and 6, *i. e.*, those with the smaller rates

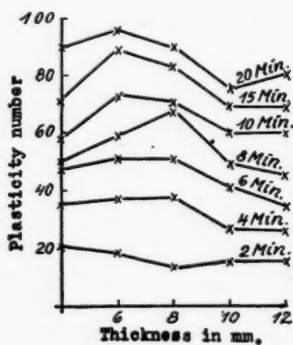


Figure 1

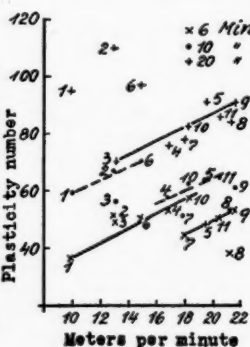


Figure 2

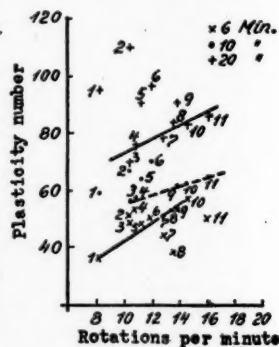


Figure 3

of rotation, behave abnormally and this time in the opposite sense. They therefore give more plastic rubber than that corresponding to their rates of rotation. Judged by these values, no influence of the frictional ratio is evident; at the most it might possibly be concluded from the results on mills 2 and 3 and on 8 and 9, which had about the same rates of rotation but different frictional ratios, that the mills with the higher frictional ratios showed the less masticating effect. Later in a discussion of theories of mastication, the possible significance of this fact will be dealt with.

As a third factor there is the temperature of the mills. On this point reference may be made to earlier results⁵, so that here I shall merely call attention to this work. It should be pointed out, however, that the temperature coefficient was 0.05, *i. e.*, for a temperature rise of 20° C. the plasticity increased two-fold.

Let us now compare these results with those of other investigators. In the work of Talalay,⁴ for instance, the most important results are surveyed. As for the load on the mill, it may be concluded from the very interesting results of Griffith⁶ that, with increasing opening between the rolls and increasing size of batch, the temperature reached after a definite time of mastication increases. Since, however, according to Griffith this temperature is inversely proportional to the work performed by the mill in order to reach a given plasticity, the same

conditions exist as in my own experiments, *i. e.*, the smaller the load, the greater the extent of mastication.

For comparison of the influence of the mill constants, we have only the work of Zimmermann,⁷ in which the author found a rise in temperature but no change in the plasticity with an increase in the circumferential speed of the rolls and the frictional ratio. It may be assumed that these results, which are at variance with my own, can be explained on the one hand by the use of the relatively insensitive parallel-plate plastometer, and on the other hand by the fact that the circumferential speed and not the rate of rotation was used in the calculation. Moreover it is of great importance that these observations were carried out, not with crude rubber, but with tire tread mixtures. The values may thus be completely altered by the well-known coagulating effect of American gas black.

Finally the influence of the temperature remains to be considered. As has been recently shown,⁸ this is always an important problem, and apparently is closely related to the problem of how rubber behaves when heated. The other problem as to how this heated rubber can be further worked is a secondary one, but is of importance if the subject is to be considered as a whole. In a study of the individual factors, however, the first problem is the one which is the more in order. It might be said briefly that, according to the results available up to this time, plasticity is proportional to the energy consumed in mastication, in fact to the mechanical as well as to the heat energy. In view of this, it is obvious that in plasticity determinations the rubber is brought to the same temperature at which it was during mastication. In this respect I hold a view at variance with that of Vogt⁹ and in agreement with Schidrowitz,¹⁰ who some years ago emphasized that it is more accurate to masticate rubber according to energy than to time.

How Shall We Represent the Process of Mastication?

Lunn,¹¹ who was probably the first to develop the ideas of Fessenden, described the rubber structure, and assumed that during mastication the shell of the globules becomes torn, thus allowing the viscous contents to flow out from the inside. Experiments by Freundlich and Hauser¹² have confirmed this view. Klein and Stamberger¹³ and Grenquist¹⁴ reached similar conclusions in their work, and showed by microscopic observations that with increasing degrees of mastication the number of the ultra-microscopic particles increases. More recently an entirely different theory has been proposed which gives to oxygen a decisive roll in the process of mastication. In particular, Cotton¹ and Busse,¹⁵ on the basis of very extensive experiments, have shown that in the presence of oxygen the process of mastication is much greater than when the rubber is masticated in an atmosphere of nitrogen or carbon dioxide. Then again Dufraisse¹⁶ has taken the stand that oxygen is a determinant factor in the softening of rubber during mastication.

In view of all this and also in view of my own experiments, I shall now endeavor to judge both sides of the two theories, disaggregation and oxidation, and from this consideration to form a concept of the whole process. It is clear that the works of Cotton and of Busse support the oxidation theory, but I wish to present the following in contradiction. As early as 1929 I carried out experiments in a small, enclosed mixer (Werner-Pfleiderer) in the same way as did Cotton, without finding any differences in the action of the different gases. At that time I used one kilogram of rubber, and let the particular gas pass slowly through the apparatus during the experiment. The chief difference between this and the technic of Cotton consists therefore first of all in the larger quantity (Cotton used only 300 grams for each experiment) and secondly in the smaller concentration of the gas.

Cotton mentions a pressure of 7 to 14 centimeters of water, and just this difference between the concentration of the gas and that of ordinary mastication makes it appear doubtful to me whether the conclusion can be drawn that mastication is an oxidation. To me there is no doubt that with the help of oxygen or, better expressed, with oxidation products which are formed it is possible to plasticize rubber more rapidly than when milling is carried out in inert gases. However, it might be well to consider how much lower is the concentration of oxygen, calculated upon 1 gram of the rubber, during the normal milling process than it is in the experiments mentioned above. Moreover, the fact should not be overlooked that the determination of the plasticity was carried out at a much lower pressure than in my own investigations. As I have already been able to show,² the influence of the nerve is taken into consideration in my method, whereas in the method of Cotton it is disregarded in spite of its playing an important part in this case.

We now come to the process of mastication. As it has always been found experimentally, this process involves as an initial step an extensive breakdown of the rubber, resulting in a great increase in the plasticity, which is followed by a gradual lessening of the break-down effect upon further milling. This does not, in my opinion, conform with a purely oxidation process, which would proceed more uniformly, and would die out only when the rubber was completely oxidized, that is, when it had become sticky. On the other hand, if the theory of disaggregation is assumed to be correct the explanation is simpler. First of all there is a rupture of the rigid structure, for which a great expenditure of energy is necessary. Upon further milling the particles, part of which have now become mobile, act as a buffer so that further progress of disaggregation is only gradual. Moreover, the fact that it is not the time but the energy consumed that is the determinant factor in bringing about mastication can be explained more simply by the mechanical theory. The fact that the temperature coefficient is positive is in harmony with both theories. There must be taken into consideration the fact that raw rubber is not so easily attacked by oxygen as is vulcanized rubber,¹⁷ and finally the recently published work of Dogadkin and Balandina,¹⁸ which uses the gold reaction as a measure of oxidation, shows that upon milling on cold rolls there is only slight oxidation, that upon hot mastication there is in general no oxidation, and that it likewise disappears upon longer milling.

Considering the various observations as a whole, the following conclusions may be drawn. On the first passage of the rubber through the rolls, the rigid mass is stretched and then ruptured. In this way the shells of the latex particles burst, in so far as this has not already taken place during the preparation of the crepe at the plantation, and the gel flows out from the inside. With the second passage through the rolls, the bonds of the micelles are stretched and then torn, and since the rapid stretching is an exothermal phenomenon¹⁹ and the rubber is a poor conductor of heat, the temperature of the system rises rapidly with repetition of the procedure, and the rigid structure gives place to a very mobile mass, which yields under pressure, without the limits of adhesion between the individual micelles being reached, as in the first state. In other words, there is first of all a destruction of the nerve, followed by plasticization by the heat generated, without the nerve being any further degraded. This thermal plasticity is reversible, whereas the mechanical plasticity is irreversible, or expressed differently, recovery depends only upon the temperature equalization and upon the stresses which originate from this. We are now in a position to explain also the action of the factors which were mentioned at the beginning. As for the first factor, the load on the rolls, no further

explanation is necessary. If we turn next to the third point, the influence of the temperature, it is also clear here that a rise in temperature increases the mobility of the micelles, and therefore increases the thermal plasticity.

The influence of the mill constants still remains to be discussed. On the basis of the mechanical theory, the effect of milling must increase with an increase in the speed of rotation. However, as a result of the repeated stretching, the temperature rises and, according to factor two, the system is in this way rendered more mobile, and this works counter to an increase in mechanical plasticity. The greatest injury to the nerve must therefore take place with a low number of revolutions per minute of the rolls, since in this case cooling can take place better. In fact, mills 1, 2, 5, and 6 in Table III and Fig. 3 show the highest plasticity values. As far as the frictional ratio is concerned, we have already seen from the data for mills 2 and 3 and for 8 and 9 that a higher frictional ratio does not give greater plasticity, but rather that there is a tendency to have the opposite effect. This is again due to the greater increase in temperature which is caused by the greater frictional ratio, so that the rubber is more highly stretched in this case.

As has been seen from the experiments, in order to make rubber plastic and suitable for further working on a calender or in a tube machine, part of its nerve must always be destroyed. This is not possible with thermal plasticization because of the danger of premature vulcanization, and there is no accelerator known today which may be said to commence to act at 125° C. and reach full activity within a few degrees. In my opinion the development of such a substance should be an important objective, because it is inconsistent to destroy even partially a property that is so highly valued.

Another way to make rubber plastic is by the addition of softeners. Naturally we are interested here only in true softeners. According to the classification of Burbridge²⁰ pseudo-softeners, to which, for example, fatty acids belong, are really dispersing agents, and develop their complete activity only in loaded mixtures. According to Burbridge, true softeners are swelling agents for rubber, which do not destroy the cohesion of the micelles, and therefore they do not break down the nerve. In this group bitumen, pine tar pitch, benzine, naphthalene, and in my opinion some factices, should be included. The development of such substances should likewise receive attention. These should not, as has been customary with oils up to now, be mixed with the fillers, but must be added directly with the rubber during its mastication. In this connection, attention must be called again to the work of Cotton.¹ In his experiment on milling with oxygen, the softeners were in an ideal state of dispersion in the rubber during the process. The work of Ungar and Schidrowitz (English patent 368,902) for the preparation of so-called softened rubber depends upon a similar process. If in this case the oxidation can be so controlled that only the impurities in the rubber are changed and the nerve is not destroyed, perhaps it is also a step forward in the direction suggested above by me.

In conclusion, a few words may be said about the measurement of plasticity. As I have already mentioned in the beginning, there is probably no longer any doubt that the method of Marzetti is the most accurate one. If in spite of this the parallel-plate method is so much used, it is because of its greater convenience and its somewhat greater speed of performance. However, with a well constructed Marzetti plastometer, the loss of time will be very slight. Another objection which is always raised is that none of the methods up to now permits the measurement of the plasticity of the substance while it is being milled. This is today no longer a sound objection, for if the changes in the plasticity with pressure and tem-

perature are known exactly, it is not necessary as formerly to wait a definite length of time, but measurements can be made immediately and values under constant conditions can be calculated from these measurements.

As in my earlier work I have attempted in the present work to present problems which might be of great interest to the whole rubber industry. At this time I have not the opportunity to carry these studies further, and I should therefore like to ask whether these problems do not warrant more extensive investigation by a research laboratory. Unfortunately there is no such institute in Germany, and it is very much to be regretted that the German rubber industry has not up to the present day united on a common basis and created such a center of research. While other branches of industry have recognized long ago the importance of such an institute, the rubber factories still consider scientific study a luxury. It should be superfluous to point out that science and practice must coöperate if progress is to be made in an economic respect as well as in an understanding of the nature of the problems.

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Plastic and Elastic Phenomena in Rubber*

A. van Rossem

1. Introduction

Before considering plastic and elastic phenomena in rubber, a brief theoretical introduction may be given to make clear the various concepts involved.

If in any material a shearing stress t produces a rate of shear dv/dy , the relation between this rate and the stress can be expressed by the following general formula:

$$\frac{dv}{dy} = \left(\frac{t - f}{\eta} \right)^n$$

where f is the critical shearing stress below which no deformation occurs, and n and η are constants (see, e. g., Scott, *Trans. Inst. Rubber Ind.*, 7, 169 (1931)).

Various particular cases can be deduced from the above, as follows:

I. $f = 0$; $n = 1$; whence $\eta dv/dy = t$. This is the case of pure viscous flow, where deformation (shear) occurs even under an infinitesimal stress, and the rate of deformation is proportional to the stress; η is in this case the viscosity.

II. $n = 1$; whence $\eta dv/dy = t - f$. This represents ideal plastic flow (Bingham, "Fluidity and Plasticity," New York, 1922). Deformation first occurs when the shearing stress reaches a critical value f (yield value), and the slope of the straight line obtained by plotting dv/dy (vertically) against t (horizontally) represents what Bingham terms "mobility." In practice, however, this line is seldom straight, but is partly or wholly curved.

III. $f = 0$; whence $\eta^n dv/dy = t^n$. The graph of dv/dy plotted against t is in this case a curve.

Now in the case of rubber we are concerned not only with viscosity and plasticity, but also with a third and very important phenomenon, viz., elasticity. When a body, under the influence of a force, undergoes a deformation which disappears instantaneously on removing the force, this deformation is termed purely elastic. Generally, however, bodies show not pure elasticity, but a complex combination of elasticity and plasticity.

Bingham (*J. Franklin Inst.*, 197, 99 (1924)) describes this combination as follows: When a force (e. g., pressure) acts on a body there occurs first an instantaneous deformation ("elastic deformation"). If the force is great enough and continues to act, an increasing proportion of the structural elements of the material begin to flow, giving rise to a curved portion on the time/deformation diagram ("pseudo-plastic flow"). When all the elements are undergoing flow the time/deformation curve becomes linear ("plastic flow"). If now the deforming force is removed a part of the deformation disappears instantaneously ("elastic recovery"). For a certain period after this the recovery continues at a decreasing rate ("elastic after-effect" or "pseudo-elastic recovery"), and finally there remains a certain permanent deformation ("plastic deformation" or "permanent set"). In practice, however, the "elastic recovery" does not equal the "elastic deformation" as might be expected.

* *De Ingenieur*, 1934, Nos. 38 and 42; from a lecture given before the "Stichting voor Biophysica" (Institute of Biophysics), 17th March, 1934.

2. The Rubber Industry

In considering rubber, it is first necessary to state briefly why the measurement of plasticity and elasticity is regarded as so important. Raw rubber, masticated rubber, mixed stocks, and vulcanized rubber all show elastic-plastic phenomena. Whereas in vulcanized rubber the elastic phenomena predominate, in masticated rubber and mixed stocks plasticity predominates, though all these phenomena depend considerably on the temperature. With masticated rubber it is desirable to know its plasticity, and to learn the effects of adding sulfur, fillers, and accessory materials on the plastic-elastic phenomena which it exhibits.

Plasticity measurements in the rubber industry have for some time been made (a) by subjecting the rubber to pressure between plane parallel plates and measuring the decrease in thickness, and (b) by extruding it through a small orifice and measuring the amount flowing through in unit time. (Since this lecture was given, Mooney, *Ind. Eng. Chem., Anal. Ed.*, **6**, 147 (1934) has described a third method, in which the rubber is sheared between a rotating disc and a fixed outer wall.)

3. Plasticity Measurements between Plane Parallel Plates

This method, used by Speedy (*J. Soc. Chem. Ind.*, **39**, 18T (1920)) for gutta-percha and balata, was first applied to unvulcanized rubber by Williams (*Ind. Eng. Chem.*, **16**, 362 (1924)). A modified form has been used by de Vries at Buitenzorg for raw rubbers (*Archief Rubbercultuur*, **9**, 223, 409, 446, 813 (1925); **12**, 244, 411 (1928); **13**, 283 (1929)), and by the Rijksrubberdienst, Delft, for masticated rubber and mixed stocks (van Rossem and van der Meyden, *Congrès International pour l'Essai des Matériaux*, **1927**, II, 479; *India-Rubber J.*, **76**, 360 (1928)).

At the Rijksrubberdienst the rubber test-piece is placed on a small, flat circular platform of area 1 sq. cm., so as to obtain a constant pressure (5 kg.) per sq. cm. of surface, which is not the case when no platform is used, because the surface over which the load is distributed becomes progressively greater.

The test is made at a constant temperature, usually 70° or 100° C., and a curve of thickness against time is obtained. It is usual to measure " D_{30} ," i. e., the thickness after 30 minutes under load, and at the Buitenzorg laboratory the slope of the curve is measured also.

It has been pointed out by van Rossem and van der Meyden (*loc. cit.*) that the time/thickness curve in itself does not show whether plasticity, or viscosity, or elasticity, or a combination of these is being measured. The usual practical method consisting in measuring D_{30} bears no theoretical relation to the "yield value" or "mobility" of Bingham, nor is it possible to see from the time/thickness curve whether the deformation is partly or wholly elastic.

Important theoretical work in this connection has recently been carried out by Scott, of the Research Association of British Rubber Manufacturers (*Trans. Inst. Rubber Ind.*, **7**, 169 (1931)), and by Peek, of the Bell Telephone Laboratories (*J. Rheology*, **3**, 345 (1932)). Scott succeeded in developing a theory of deformation (flow) between parallel plates, and deduced therefrom formulas for various particular cases. It is not proposed to discuss this important publication fully here, and it will suffice to mention that from the relation between $\log (dh/dt)$ and $\log h$ (where h = thickness, and t = time), the nature of the material under test, i. e., whether plastic, viscous, pseudo-viscous, etc., can be deduced (Since this lecture was given, Houwink, "Physikalische Eigenschaften und Feinbau von Natur- und Kunsthharzen," Leipzig, 1934, has applied Scott's theory to the study of synthetic

resins. This work illustrates a method of application of the theory which, in the rubber industry also, might lead to important conclusions.)

To show how it can be determined whether masticated rubber is viscous, plastic or elastic, tests were made with:

A. First latex crepe, normally milled (6 min.).

B. First latex crepe, over-milled (50 min.).

C. As A but mixed with 2½% of cobalt oleate (Stevens and Heaton, *J. Oil Col. Chem. Assoc.*, 17, 8 (1934), have shown that this considerably reduces the viscosity of concentrated rubber solutions).

A coin was laid on a disc of each of these rubbers, and left overnight at 70° C. On A the coin did not sink in; on B it had sunk partly in, while on C it had sunk much deeper, thus showing that A was plastic and B and C were viscous. When the imprint of a coin was pressed into discs of the three rubbers and these then left for 16 hours at 70° C., the impression on A remained intact, while those on B and C disappeared. By such simple tests as these it can be shown whether a material is viscous or plastic.

The question whether a material is plastic or elastic can also be answered by experiments, bearing in mind that the essential feature of plasticity is the retention of deformation after removal of the force, whereas an elastic deformation rapidly disappears. Tests have been made at the Rijksrubberdienst with a parallel-plate plastimeter, in which the force was removed after acting for 20 minutes, and the recovery measured. Experiments on masticated rubber at various temperatures showed that at 16° C. there is little plasticity; the deformation is mainly elastic (or pseudo-elastic), and thus is afterward largely eliminated by the elastic after-effect. The same applies, though in a less degree, at 30°, 45°, and 60° C. At 70° C. the elasticity and elastic after-effect are small and the deformation is largely permanent, *i. e.*, plastic. The behavior of masticated rubber thus depends considerably on the temperature, the material being essentially plastic at high temperatures while at lower temperatures elastic phenomena appear in increasing degree. The time/recovery curves, however, do not agree with the simple conception of Bingham (*J. Franklin Inst.*, 197, 99 (1924); see above), as no part of the curve representing pure elastic recovery is evident. In the observed recovery elasticity and plasticity are very intimately associated.

Using a modified plastimeter more suitable for measuring recovery, Hoekstra (*Physics*, 4, 285 (1933); *Kautschuk*, 9, 150 (1933)) has shown that:

1. Recovery is less the longer the load has acted. This may be explained on the principle that every action sets up a reaction tending to oppose it; thus, the stress causes the rubber to flow, and the longer this flow continues the more it relieves and lessens the stress, so that on removing the external force the recovery (due to the residual stress) will be less the longer the material has had an opportunity to flow. The time factor is thus very important in these phenomena, the behavior of a material under compression being largely determined by the duration of the deformation. We may express it thus: if masticated rubber is struck with a hammer it is elastic and recovers completely, but if a grain of sand be laid upon it the rubber behaves as a plastic or viscous material.

2. If two rubbers milled respectively for 8 minutes (I) and for 50 minutes (II) are put under the same compressive load for equal times, the recovery is much greater with I than with II. If, on the other hand, they are compressed to the same percentage of their original thickness the recovery is about the same in both cases. Using this latter method, Hoekstra has carried out some very important measurements of this recovery, which cannot be fully described here.

It thus appears desirable to measure recovery as a separate quantity distinct from the plasticity curve, in contrast to the proposal of Karrer (*Ind. Eng. Chem.*, 21, 770 (1929)). Karrer defines plasticity as the "susceptibility to and retentivity of deformation," and represents it quantitatively as the product of "softness" and permanent deformation, which leads to the formula:

$$P = K \frac{h - h_2}{Fh}$$

where P = plasticity, h = initial thickness, h_2 = recovery, F = shearing stress, and K = constant.

In the opinion of Hoekstra and the present writer, however, this idea is not to be commended, the separate measurement of the plasticity curve and the recovery being preferable (see also Dillon, *Ind. Eng. Chem.*, 26, 345 (1934)).

4. Elastic Phenomena in Calendering

"Recovery" is not merely a laboratory phenomenon, but a property of masticated and compounded rubber which causes no inconsiderable trouble in technical practice.

It appears in a pronounced form in the calendering process. If a circle is drawn on the sheet of stock around the middle roll, this will become an ellipse when the sheet leaves the calender; owing to elastic recovery the length decreases considerably and the width less so, while the thickness increases. This immediate contraction can be largely avoided by keeping the bottom roll cold, but if the sheet is subsequently warmed contraction will occur immediately.

This "calender effect" has been very thoroughly investigated by de Visser ("The Calender Effect and the Shrinking Effect of Unvulcanized Rubber," London, 1926).

Another elastic recovery effect noted by de Visser arises from the fact that when a sheet of stock passes between two calender rolls the surfaces in contact with the rolls are carried forward more quickly than the interior of the sheet. This sets up a strain which is retained if the sheet is quickly cooled. If a rectangular piece cut from such a sheet is now warmed, the forward edge, *i. e.*, that which passed through the calender first, will become convex in vertical section, while the rear edge will become concave. An analogous strain effect causes the lateral edges, *i. e.*, those parallel to the direction of calendering, to become concave in section when the sheet is warmed.

5. Plasticity Measurements by Extrusion through an Orifice

Measurements of the plasticity of rubber by extruding it through an orifice and weighing the extruded rubber were first carried out by Marzetti (*India-Rubber J.*, 66, 417 (1923); *Giorn. chim. ind. appl.*, 6, 277, 567 (1924)). The pressures used in these experiments, however, were much less than in modern extruding machines, and the orifice did not possess the most suitable dimensions.

An extensive research has been made by Dillon and Johnston (*Physics*, 4, 225 (1933)) using a modernized apparatus giving pressures between 4.25 and 68 kg./sq. cm.; the higher end of this pressure range corresponds to that used in modern extruding machines. The curves relating pressure with rate of extrusion at various temperatures (58° to 98° C.) were determined for a heavily compounded tread stock and for masticated rubber. With the tread stock the curves represent an almost ideal case of plastic flow, *i. e.*, the curve is a straight line starting from a point on the pressure axis corresponding to the "yield value." The latter is

independent of temperature, but the "mobility" (slope of the straight line, pressure being plotted horizontally) increases rapidly with rise of temperature. With masticated rubber there is likewise a "yield value" (somewhat dependent on temperature, however), but the curve bends strongly upward away from the pressure axis, showing that the material does not exhibit simple plasticity.

Dillon and Johnston also determined "recovery" by measuring the increase in the cross-sectional area of the rubber after leaving the orifice. Here again recovery increases as the temperature is lowered, *i. e.*, the elastic properties become more pronounced. Recovery is greater the greater the rate of extrusion, so that here, as in the experiments by Hoekstra already described, the time factor enters, the quicker the deformation the greater being the elastic recovery.

These elastic recovery effects have to be taken into account in the extruding process. Immediately after leaving the orifice the diameter of the rubber increases. Moreover, the rubber near the walls of the die is slowed down by friction, so that the velocity of the inside of the extruded cylinder is greater than that of the outer layers. If a piece of the extruded cylinder is quickly cut off it will be seen that under the influence of elastic strains arising from this difference in velocity, the forward end of the piece will become concave and the rear end convex (Barus, *Am. J. Science*, 45, 87 (1893)).

6. Plastic-Elastic Phenomena in Extension and Torsion

Bingham's conception of plastic-elastic deformation (see Section I) is of very general application, and the combination of phenomena already described is found equally in rubber subjected to stretching, twisting, or bending.

When raw rubber is stretched under a definite load there occur an elastic extension, a pseudo-plastic flow, and a plastic flow, while on removing the load a part of the deformation disappears elastically, followed by elastic after-effect, leaving finally a permanent extension which may be regarded as plasticity.

Temperature again has a great influence. Raising the temperature decreases the elastic recovery and increases plastic deformation. If a strip of raw rubber is stretched and quickly cooled the elastic recovery is very small, and most of the stretch remains. If now the stretched strip is put into warm water an enormous contraction takes place ("shrinkage").

Time has a considerable influence also; very rapid extension is mainly elastic, slow extension largely plastic.

With vulcanized rubber the elastic phenomena seem to predominate, but this is merely a question of temperature, for at low temperatures vulcanized rubber behaves in exactly the same way as does unvulcanized rubber at ordinary temperature. Thus, by cooling vulcanized rubber can be made to show "crystallization," and "shrinkage" on subsequent warming. The transition in behavior between raw rubber and vulcanized rubber is quite gradual. Gibbons, Gerke, and Tingey (*Ind. Eng. Chem., Anal. Ed.*, 5, 279 (1933)) have shown that a linear relation exists between the vulcanization coefficient and the temperature at which the rubber loses just half of its elongation when the load that produced it is removed, this temperature being higher the lower the degree of vulcanization.

The relaxation phenomenon is seen also in the stretching of vulcanized rubber. This is shown by interrupting the stretching while the stress-strain curve is being traced on a Schopper machine. When the stretching is started again the curve will first run vertically for a little way before resuming its normal course, so that the latter part of the curve will not be a continuation of the first part, but will lie

higher on the paper. If, during the interruption, the pawls on the load arm are released, the load will be seen to decrease gradually.

Finally, reference may be made to the remarkable phenomenon of the superposition of elastic after-effects; though this must occur in experiments involving stretching, it is more readily examined in torsion experiments. Kohlrausch (*Ann. Physik*, **158**, 373 (1876)) kept a rubber cord twisted through $2 \times 360^\circ$ to the right for 18 hours, then released it and twisted it 45° to the left of its equilibrium position for 30 seconds; the cord was then left to itself. The elastic after-effect now manifested itself first by a movement to the right some distance beyond the equilibrium position; the movement then reversed its direction, and the cord finally came to rest a little to the right of the equilibrium position. Kohlrausch, describing this phenomenon, remarked that the rubber behaved as though it possessed a memory.

In conclusion, some observations may be made regarding the explanation of these phenomena observed during extension.

In 1924 Katz discovered that stretched rubber shows a marked Röntgen spectrum, thus indicating that a regular orientation is set up (pseudo-crystalline condition), and there is now little doubt that the explanation of these phenomena must be related to the "crystallization" phenomena. The difficulty lies not so much in explaining the extension as in explaining elastic recovery and answering the question as to what happens when a stretched cooled rubber strip suddenly exhibits "shrinkage" owing to a rise of temperature.

It must suffice here to quote a recent theory in this connection, due to Meyer, von Susich, and Valko (*Kolloid Z.*, **59**, 208 (1932)). These investigators draw attention to the following points:

1. Numerous highly polymerized substances of very different chemical composition, *e. g.*, rubber, gutta-percha, gelatin, wool, hair, etc., show the same elastic phenomena. The explanation of these must, therefore, be independent of any given chemical constitution.

2. All these substances possess very long chain-like molecules. It may be assumed that in raw rubber these molecules are irregularly interwoven; mastication partly breaks up these chains, while calendering arranges them parallel, with a greater tendency toward crystallization. During vulcanization bridging occurs between adjacent chains, either with or without sulfur (*cf.* C. O. Weber, "Chemistry of India Rubber," **1909**, p. 92; van Rossem, *Kautschuk*, **7**, 189 (1931)). When rubber is stretched these chains are arranged more or less parallel, which explains the Röntgen interference pattern.

Regarding elastic after-effect, these investigators assume that in stretched bodies which tend to retract there exist very long main-valency chains running in the direction of stretch. A considerable part of their heat content consists of rotation and deformation motions of the individual atomic groups perpendicular to the axis of the molecule, while the valency vibrations parallel to the axis represent a smaller heat content. The lateral movements produce irregular impacts between the chains and hence a lateral repulsive force, which gives rise to the tensile stress. The temperature coefficient of this stress agrees with this kinetic conception.

How far this explanation is correct need not be discussed here; it is for the physicist to judge whether this kinetic theory really furnishes an acceptable explanation of the contraction after stretching.

Specific Volume, Compressibility, and Volume Thermal Expansivity of Rubber-Sulfur Compounds

Arnold H. Scott

I. INTRODUCTION

The specific volume, compressibility, and volume thermal expansivity of rubber-sulfur compounds¹ containing from 3 to 31 per cent of sulfur have been measured at pressures from 1 to 800 bars and at temperatures from 10° to 85° C. The results are expressed in tables, curves, and equations, so that within the indicated limits the value of any of the above properties can be readily determined for a compound of specified composition under specified conditions of temperature and pressure.

Specific volume, which is the reciprocal of the density, has been used throughout this paper, because this term is the one which is used directly in the definitions of compressibility and volume thermal expansivity. The work of Kimura and Namikawa² indicated that the specific volume of rubber-sulfur compounds at atmospheric pressure was a linear function of the temperature. The use of the specific volume thus leads to equations which are simpler than if the density is used.

II. METHOD OF DETERMINING SPECIFIC VOLUME

The specific volume of a material at atmospheric pressure was determined by means of a pycnometer. The specific volumes at other pressures were obtained from measurements of the changes in length of a rod of the same material when subjected to different pressures.

The procedure used in the determination of the change in length was to make measurements at successive pressures through a pressure cycle at a fixed temperature. The pressure was increased in steps of 200 bars³ up to 800 bars, allowing time for temperature equilibrium in each case. The same measurements were then made as the pressure was decreased by steps of 200 bars back to atmospheric pressure. A group of measurements obtained when carrying the specimen through this pressure cycle is called a set of data. A repetition of this at the same or another temperature is considered another set.

The specific volume at a given pressure was computed from the change in length of the rod when the pressure was applied. Assuming the material of the rod to be isotropic, then the volume change with pressure is proportional to the cube of the length.⁴ Let

L_a = the length of the rod at atmospheric pressure (approximately 1 bar)

ΔL = the change in length of the rod when the pressure has been increased to any pressure, say P bars

V_a = the specific volume at atmospheric pressure (approximately 1 bar)

V = the specific volume at P bars

Then

$$\frac{V}{V_a} = \frac{(L_a - \Delta L)^3}{L_a^3}$$

or

$$V = V_0[1 - 3\Delta L/L_0 + 3(\Delta L/L_0)^2 - (\Delta L/L_0)^3] \quad (1)$$

The last term was found to be negligible for pressures used in this investigation.

The specific volume was found to vary with the pressure in a manner described by the equation:

$$V = V_0(1 + \alpha P + \beta P^2) \quad (2)$$

where P is the pressure in bars, V_0 is the specific volume at zero pressure, and α and β are characteristic coefficients which depend on the temperature and the composition of the rubber-sulfur compounds.⁵ V_0 is equal to V_∞ within experimental error and therefore V_∞ is used in the above equation in place of V_0 . The approximate values of the coefficients may be obtained from measurements of change in length by selecting two observations from a set, preferably the change in length at maximum pressure and the change in length at about one-half maximum pressure. Let

$$\begin{aligned} V_1 &= \text{specific volume at } P_1 \text{ bars} \\ V_2 &= \text{specific volume at } P_2 \text{ bars (about 2 times } P_1) \\ \Delta L_1 &= \text{change in length from 1 to } P_1 \text{ bars} \\ \Delta L_2 &= \text{change in length from 1 to } P_2 \text{ bars} \end{aligned}$$

Then from Equation 2:

$$\begin{aligned} V_1 &= V_0(1 + \alpha P_1 + \beta P_1^2) \\ V_2 &= V_0(1 + \alpha P_2 + \beta P_2^2) \end{aligned}$$

and from Equation 1, neglecting the cubic term:

$$\begin{aligned} V_1 &= V_0[1 - 3\Delta L_1/L_0 + 3(\Delta L_1/L_0)^2] \\ V_2 &= V_0[1 - 3\Delta L_2/L_0 + 3(\Delta L_2/L_0)^2] \end{aligned}$$

Solving these equations we find:

$$\alpha = \frac{3}{P_2 - P_1} \left\{ \frac{P_1}{P_2} \left[\frac{\Delta L_2}{L_0} - \left(\frac{\Delta L_1}{L_0} \right)^2 \right] - \frac{P_2}{P_1} \left[\frac{\Delta L_1}{L_0} - \left(\frac{\Delta L_2}{L_0} \right)^2 \right] \right\} \quad (3)$$

$$\beta = -\frac{3}{P_2 - P_1} \left\{ \frac{1}{P_2} \left[\frac{\Delta L_2}{L_0} - \left(\frac{\Delta L_1}{L_0} \right)^2 \right] - \frac{1}{P_1} \left[\frac{\Delta L_1}{L_0} - \left(\frac{\Delta L_2}{L_0} \right)^2 \right] \right\} \quad (4)$$

The values of α and β obtained from these equations for a given specimen were used in Equation 2, and the resulting equation was then checked against all the values of the specific volume of this specimen, determined from its change in length. A slight revision in the values of the coefficients was necessary in a few cases in order to make the equation more closely represent the complete data of a set.

Compressibility, σ , is defined as the decrease in volume per unit volume for a unit increase in pressure at constant temperature. That is

$$\sigma = -\frac{1}{V_0} \frac{dV}{dP} \quad (5)$$

Thus by differentiating Equation 2 we obtain

$$\sigma = -\alpha - 2\beta P \quad (6)$$

The compressibility may be determined by simply giving α and β the values computed from the equations above.

The volume thermal expansivity is defined as the increase in volume per unit volume for an increase of 1° of temperature at constant pressure. Since the volume thermal expansivity was determined only for those temperature ranges in which the specific volume was a linear function of the temperature, the expansivity was computed from the slope of the line obtained by plotting the specific volume against the temperature.

III. DESCRIPTION OF APPARATUS

The specific volume measurements at atmospheric pressure were made with the pycnometer described by Ashton, Houston, and Saylor.⁶ A sketch of this pycnometer is shown in Fig. 1. The pycnometer was made of glass and had a capacity of about 25 cm.³

The specific volume was determined from the weight of the specimen and the weight of the pycnometer containing first the confining liquid and then the confining liquid and specimen. Water was used as the confining liquid. Investigation showed that the absorption of water by the rubber-sulfur compounds had a negligible effect on the results. The height of the confining liquid in the capillary tube was adjusted after the pycnometer and contents had been kept in a constant temperature bath for 30 minutes to assure a uniform temperature. The bath was controlled to 0.1° C. and weighings were made to 1 mg. After adjustment at the desired temperature, the pycnometer and its contents were brought to a temperature near that of the room before it was weighed. This was done by placing it in a water bath at room temperature for a few minutes.

No grease was used on the ground-glass joints of the pycnometer and therefore slow evaporation of the water took place, making the weight a function of the time which elapsed after the liquid was adjusted in the capillary tube. However, a strict time schedule was employed so that measurements could be repeated to 5 mg. or less, which resulted in an error of less than 0.1 per cent in the determination of specific volume.

The specific volume, in most cases, was also determined at 25° C. on the entire specimen used in the pressure measurements. This was determined by weighing the specimen in air and in water.

The change in length of a specimen with pressure was determined with the apparatus shown diagrammatically in Fig. 2. The specimen, which was inclosed in the pressure chamber, was suspended at its upper end. The glass scale which was fastened to the lower end extended between the two glass pressure windows. The scale was illuminated through one window and viewed by means of a microscope through another window.

The pressure chamber consisted of a steel pipe known commercially as "double extra heavy," having a heavy fitting on each end. The upper fitting had two openings, one of which allowed the insertion of the specimen and the other the connection to the pressure pump. The lower fitting had two openings which were opposite each other and into which the steel plugs carrying the pressure windows

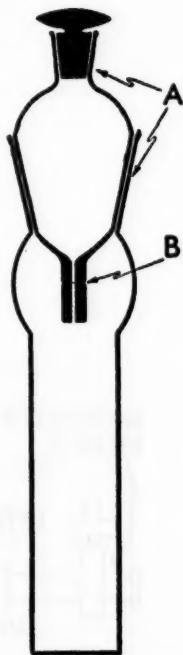


Figure 1—Apparatus for Specific Volume Determinations at Atmospheric Pressure

A, ground glass joints; B, volume adjustment mark.

were screwed. The fittings were equipped with lead rings which could be firmly pressed into the threads by means of set screws, thus producing tight joints.

The pressure chamber was hung from a bracket on a brick wall. This bracket had a flat horizontal iron shelf about 9 mm. thick from which was cut a U-shaped section of such size that the plug in the upper end of the pressure chamber would just fit into it. Thus the weight of the chamber was supported by the shoulder of the plug resting on the shelf. The microscope used to view the scale was mounted

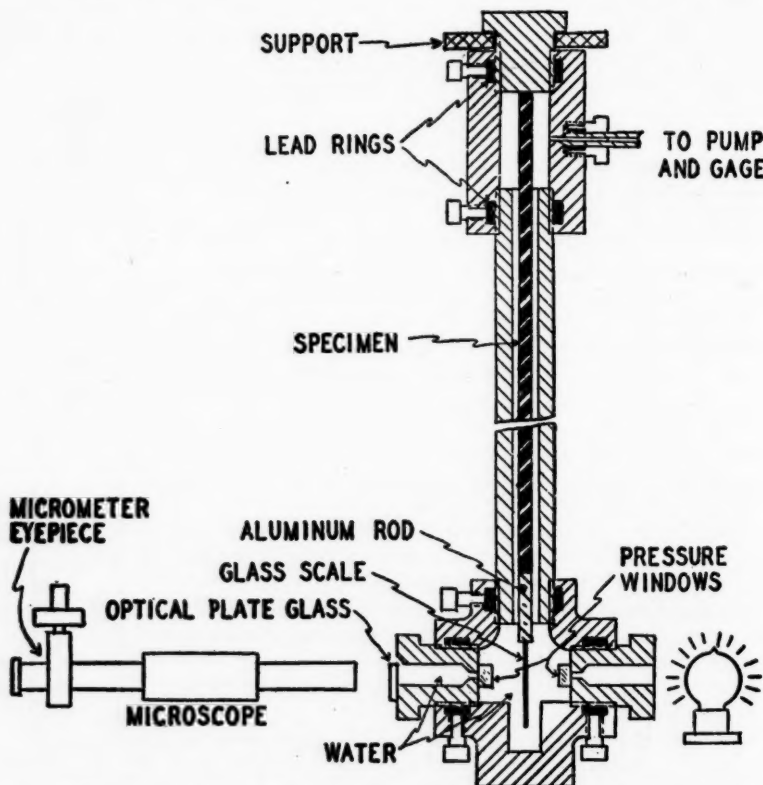


Figure 2—Apparatus Used in the Determination of the Change in Length of a Cylindrical Specimen with Pressure

on another bracket which was also fastened to the brick wall. Since a set of measurements was made at constant temperature, the distance between the brackets was assumed to remain fixed during this set of observations. Any changes in dimensions of the pressure chamber due to pressure changes had no effect on the measurement of the length of the rubber rod. A prism which was mounted on the bracket with the microscope and which is not shown in the figure was used, so that the microscope could be mounted at right angles to the line through the pressure windows. This allowed the operator to make observations while facing the wall, and kept the face of the observer out of danger in case the pressure window failed. The lower end of the pressure chamber was held against two guides by spring clips not shown in the figure.

The rods of soft rubber were fastened to the plug at the upper end by cementing them with a commercial thermoprene cement. The rods of hard rubber were screwed to the plug. A machine screw about 6 mm. long was fastened to the end of the plug. A hole was drilled and tapped in the end of the rod and this was then screwed onto the machine screw. Some of the semihard rubbers were both screwed and cemented to the plug.

An aluminum rod 17 cm. long was fastened to the lower end of the rubber rod by

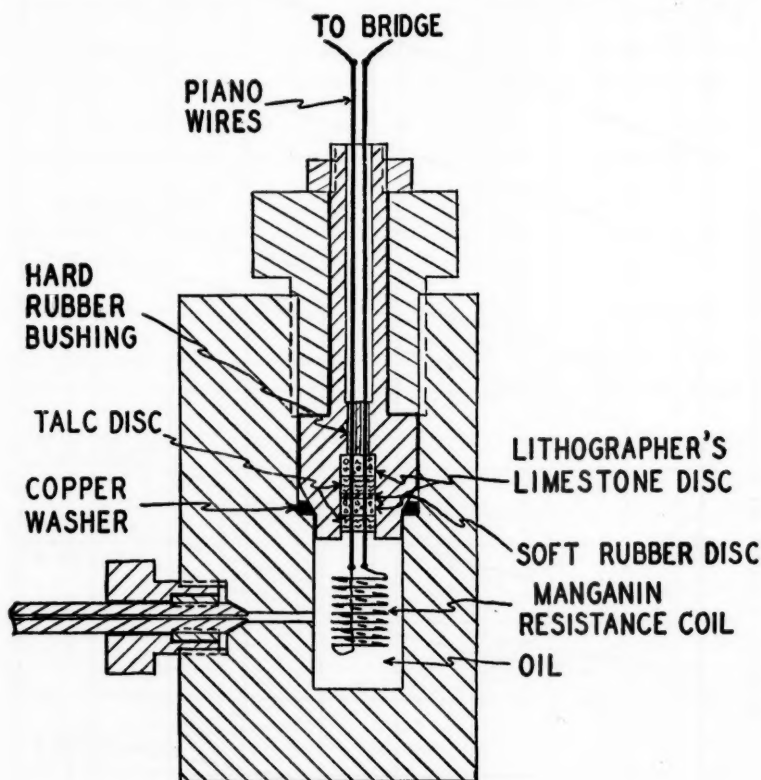


Figure 3—Resistance Pressure Gage

the same method used to fasten the rod to the plug. This metal rod was necessary because the density of some of the soft rubbers was less than that of water, and a weight was needed to counteract the tendency of the rod to float. An aluminum rod having a weight sufficient to supplement the weight of the least dense specimen was used on all specimens. The excess weight of the metal rod for the more dense specimens did not affect the measurements appreciably, since this excess weight was small and the stiffness of the rubber specimens increased with the density.

The engraved glass scale, which was 3 cm. long, was fastened to the lower end of the aluminum rod by means of a frame and clip. The clip kept the end of the scale pressed firmly against the end of the rod. The changes in position of the scale were due to changes in length of both the rubber and aluminum rods. The

small corrections for the change in length of the aluminum rod were computed from the values of compressibility given in the International Critical Tables.⁷

The scale was ruled with a diamond point on the platinized surface of a piece of optical plate glass. Since the scale was illuminated from behind, the lines

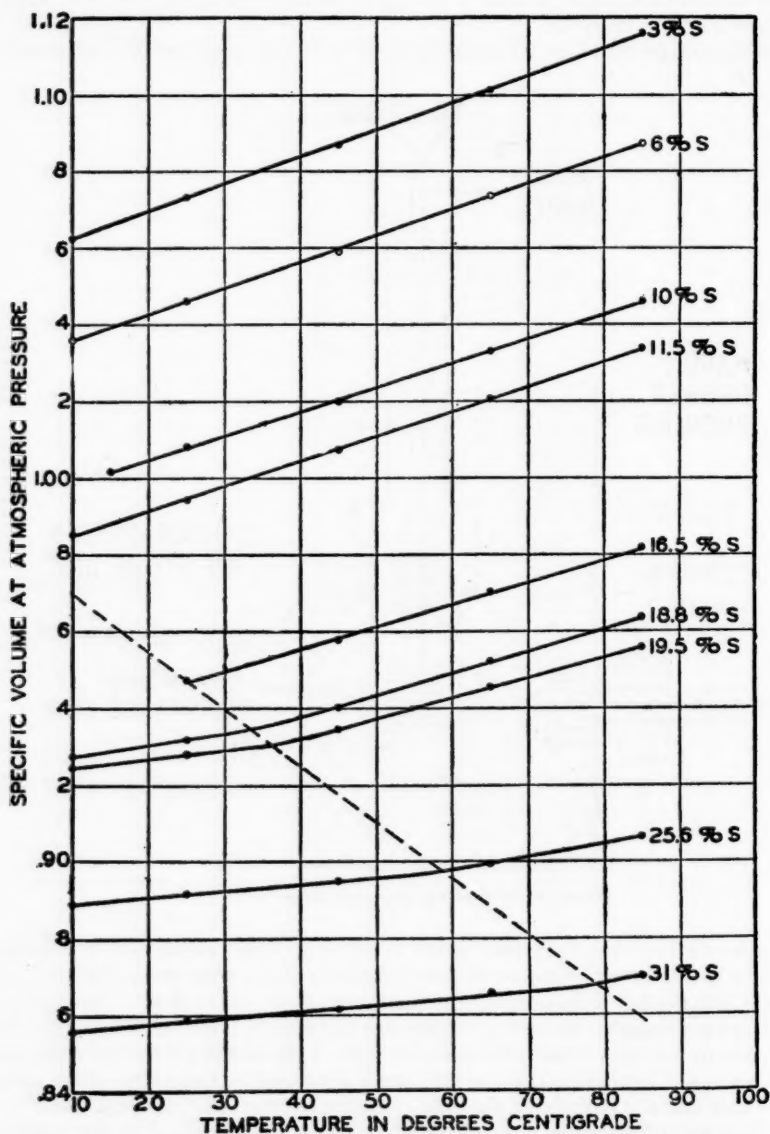


Figure 4—Effect of Temperature on the Specific Volume of Rubber-Sulfur Compounds at Atmospheric Pressure

The values represented by open circles were obtained by interpolation when the specific volumes were plotted against the percentage of combined sulfur.

appeared bright on a dark field. The lines were ruled on a precision dividing engine at 0.5 mm. intervals, and were designated by engraved numbers. This scale was used to calibrate the micrometer eyepiece of the microscope. One millimeter was equivalent to 346 divisions on the micrometer eyepiece.

The motion of the scale and hence the change in length of the specimen was measured by means of the micrometer eyepiece of the microscope. Three lines

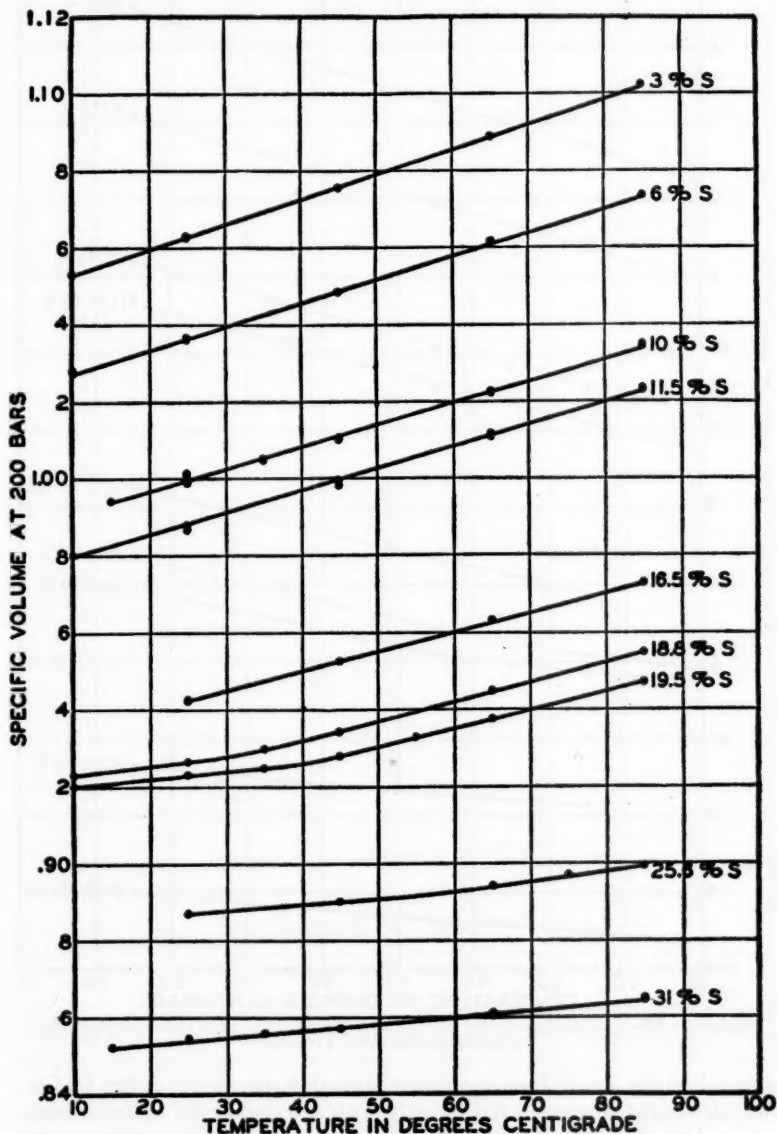


Figure 5—Effect of Temperature on the Specific Volume of Rubber-Sulfur Compounds at 200 Bars' Pressure

of the scale were visible in the field of the microscope. The crosshair was set on the line nearest the center of the field and the change in length of the rod was determined from the reading of the micrometer eyepiece and the number of the line on the scale. The approximate total length was obtained from the same

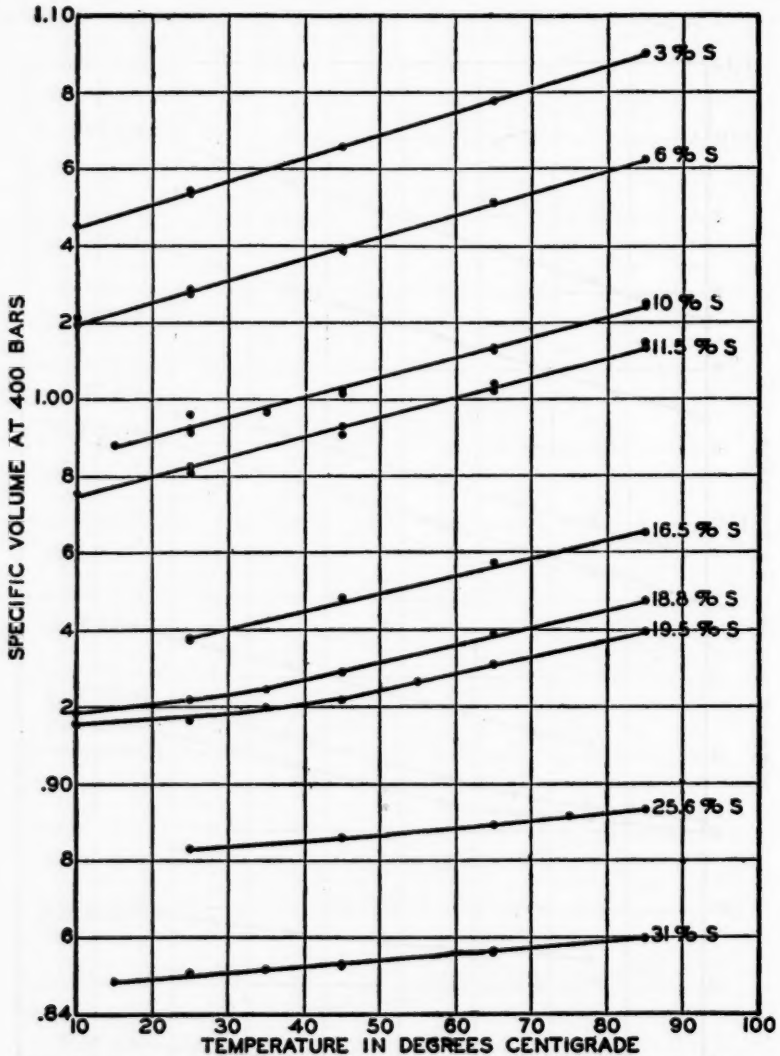


Figure 6—Effect of Temperature on the Specific Volume of Rubber-Sulfur Compounds at 400 Bars' Pressure

readings since the length from the upper support to the center of the field of view of the microscope was measured directly with a meter stick. This distance was determined to 0.5 mm. and the length of the specimen was obtained by subtracting from this the length of the metal rod and scale above the center of the field of view.

The glass pressure windows were supported by hardened plugs of stainless steel each of which had a hole bored through its center. The diameter of this hole was 6 mm. at the inner end of the plug where it was covered by the window. This was increased to about 15 mm. at the other end of the plug. The seal be-

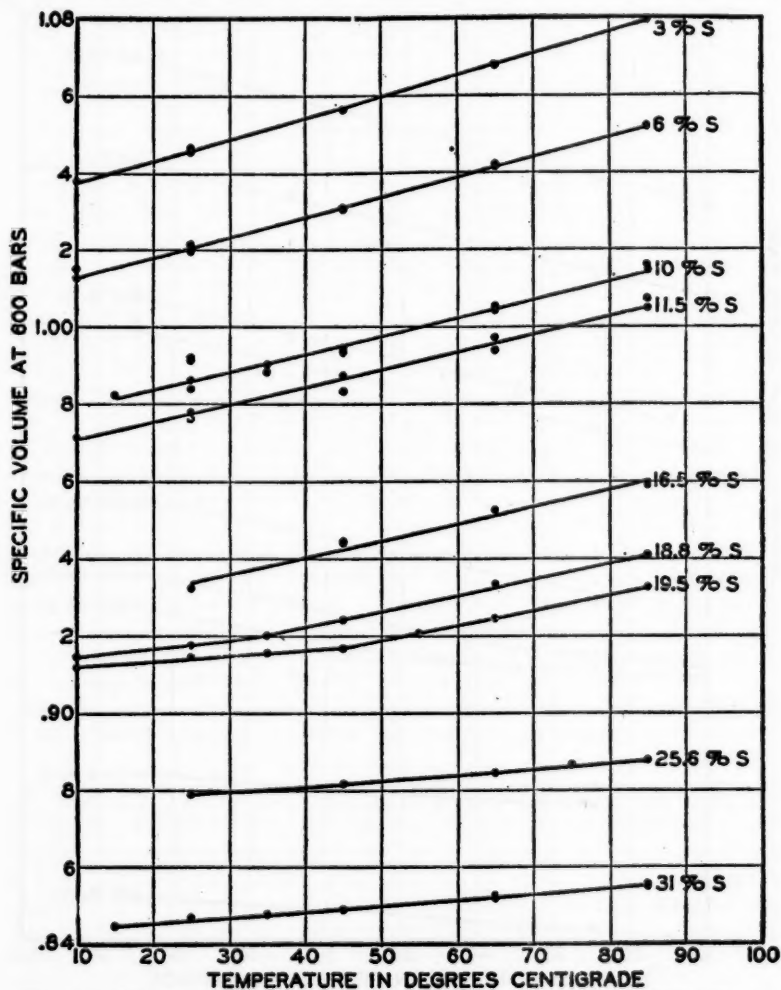


Figure 7—Effect of Temperature on the Specific Volume of Rubber-Sulfur Compounds at 600 Bars' Pressure

tween the glass and the steel plug was made by grinding the two surfaces optically flat, allowing the pressure of the liquid to force the glass firmly against the steel. This effectively sealed the joint since the bearing surface was appreciably less than the surface exposed to the pressure. It was necessary to put a thin film of Canada balsam under the window to hold it in place until the pressure was applied.

Water was placed in the opening of the plug through which the scale was viewed. This was done to minimize the distortion of the field of view in the microscope due

to warping of the glass window under pressure. The water had an index of refraction which was much nearer that of the glass than was that of air. Therefore the refraction at the water-glass surface was much less than that at an air-glass surface, making the effect of the warping of the window on the field of view less

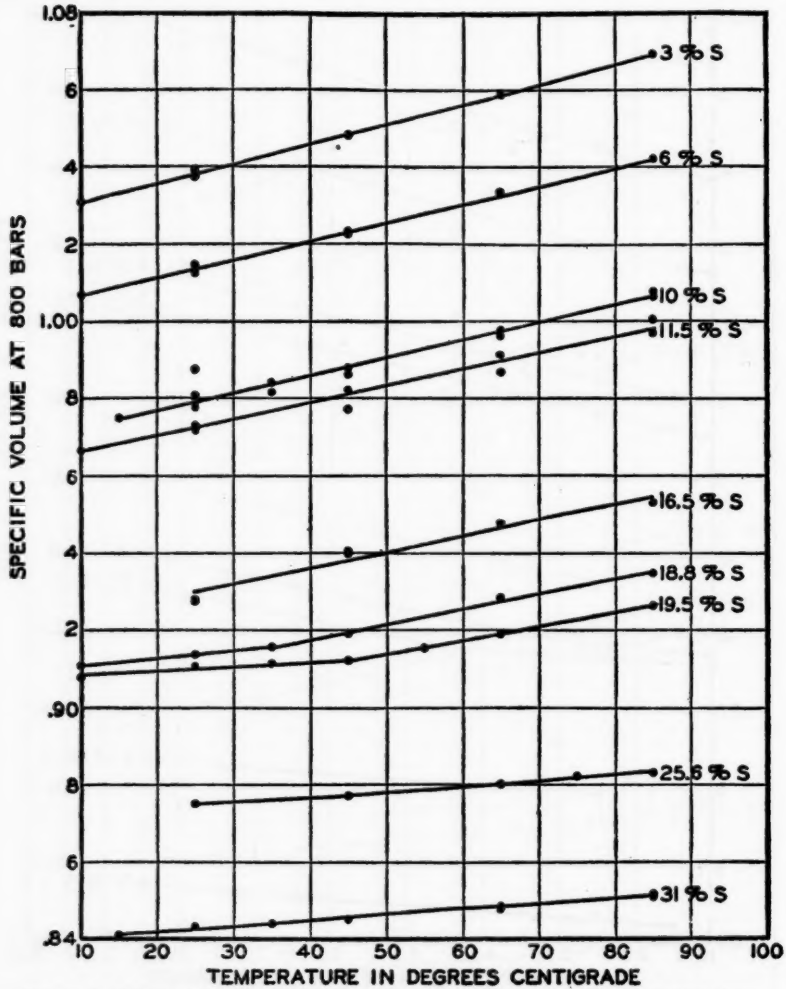


Figure 8—Effect of Temperature on the Specific Volume of Rubber-Sulfur Compounds at 800 Bars' Pressure

when the window was surrounded with water. In fact, surrounding the window with water reduced the change in refraction due to warping of the window to such an extent that it was found to be negligible for the pressures used in this investigation. A piece of optical plate glass was cemented over the opening at the outer end of the plug to keep the water in place and to give a refracting surface which was not affected by the pressure.

The pressure chamber was mounted in a constant temperature air bath provided

with numerous baffles and valves so that the air flow could be readily changed and the same temperature could be maintained throughout the pressure chamber. The temperature of the chamber was measured by 3 thermocouples soldered to it, one near the top, one near the middle, and one at the bottom. It was possible, with close watching, to keep the temperature of the chamber as indicated by the 3 thermocouples within 0.1°C . of the desired temperature.

The pressure was measured by a resistance gage of the type described by Gibson.⁸ A diagram of this gage is shown in Fig. 3. The manganin resistance coil was placed in a steel chamber which was connected to the pressure chamber by small-bore steel tubing. The leads to the coil were made of piano wire and were brought out through a packing of limestone, rubber, and talc. The limestone and talc were machined to a tight fit. The rubber was made oversize and had to be squeezed into place. The whole packing was forced into place with a pressure of several thousand pounds. To do this a piece of steel was made to hold the plug and a plunger was made to place over the packing. This was then placed in a press and the packing forced into place. The packing was kept in place by the friction against the sidewalls. Pressure applied to the gage chamber forced the packing closer into the plug opening and more effectively sealed it. There was no tendency for the lead wires to creep with this method of packing.

The coil was made of No. 38 manganin wire, and had a resistance of about 101 ohms. It was wound in a single layer on a light cylinder of very thin paper. The form was preserved by covering the coil with a thin coat of shellac and baking it in an oven for several hours. The coil was seasoned under a pressure of 8000 bars. A light insulating oil was used as the pressure medium surrounding the coil. Since water was used in the rest of the pressure apparatus it was necessary to put a U-tube filled with mercury in the pressure line leading to the gage.

The resistance of the coil was measured with a Wheatstone bridge capable of measuring resistance to 0.0001 ohm. The gage and bridge were placed in a carefully controlled temperature bath of oil. A change in pressure of 1 bar changed the resistance of the coil about 0.0002 ohm so that a change in pressure of $1/2$ bar could be readily measured. Twenty to thirty minutes were allowed after the pressure had been applied for conditions to reach equilibrium before measurements were made, since a change in pressure affected the temperature equilibrium.

IV. PREPARATION OF SPECIMENS

The specimens were made from purified rubber and sulfur, and were molded in the form of rods about 1 cm. in diameter and 85 cm. long. The sulfur content of the different specimens ranged from 3 to 31 per cent, with no interval greater than 6 per cent. The specimens were analyzed for sulfur content after they were vulcanized. The sulfur content was determined by burning a weighed sample of the rubber in a bomb with oxygen, absorbing the products of combustion in an alkaline solution, and determining the sulfur as barium sulfate as described by Mease.⁹

The purification of the rubber and the mixing of the rubber and sulfur were carried out as described in a former paper.¹⁰ The specimens were vulcanized in a mold in steam at 148°C . for about 20 hours. This relatively long time of vulcanizing was for the purpose of bringing practically all the sulfur into combination with the rubber.

The specimens were carefully examined for porosity. The density of the rod as a whole was determined by weighing it in air and in water. Any rod which had a density appreciably less than the value to be expected from previous experience with specimens of similar composition was discarded.

V. RESULTS

The determinations of the specific volume are divided into two groups, those which were obtained with the pycnometer at atmospheric pressure and those which were obtained from the measurement of the change of length with pressure. The determinations at atmospheric pressure with the pycnometer were much more accurate and reproducible than those made under pressure. These results and the compressibility are presented in the form of curves. The values of the volume thermal expansivity are given in a table.

1. Specific Volumes at Atmospheric Pressure

The values of the specific volumes at atmospheric pressure for various percentages of sulfur are shown in Fig. 4, where they are plotted against the temperature. The specific volume of the specimen containing 6 per cent of sulfur was measured directly at 25° C. only. The values at the other temperatures, as indicated by open circles, were obtained by interpolation when the specific volumes were plotted against the percentage of sulfur for each temperature.

The relation between the specific volume and temperature is linear for specimens containing up to 16.5 per cent of sulfur. The relationship for specimens containing higher percentages of sulfur is such that the curve is linear in two sections but the slopes of the two sections differ. The slope for the higher temperatures is about that for the specimens containing 16.5 per cent of sulfur or less. Thus it is seen that if a line is drawn from approximately 0.97 at 10° C. to approximately 0.86 at 85° C., as shown in the figure, the curves or parts of curves above this line all have about the same slope and the parts of curves below this line have about the same slope, but the slope of the latter is different from the slope of the curves above the line. This was also observed and reported by Kimura and Namikawa.¹¹ Bekkedahl¹² reported changes in slope of the curves for 2, 4, and 6 per cent of sulfur at low temperatures.

2. Specific Volumes at High Pressures

The specific volumes at 200, 400, 600, and 800 bars' pressure are shown plotted against the temperature in Figs. 5 to 8. These values were obtained from measurements of the changes in length of the specimens under pressure. These curves have the same general form as those at atmospheric pressure, being merely shifted in position. The spread of the points increased with the pressure, in some cases making the determination of the slope more difficult for the higher pressures. However, it was readily determined that the slope of all the curves decreased with pressure, which means that the volume expansivity decreased with pressure. Each curve was shifted to lower values of specific volume as the pressure was increased. The amount of the shift was greater for the low percentages of sulfur than for the high percentages. The line marking the boundary between the curves or parts of curves having the smaller slopes and those having the larger slopes shifted to lower values of specific volume as the pressure was increased. At 800 bars the approximate position of this boundary line was from 0.94 at 10° C. to 0.84 at 85° C.

The manner in which the specific volume decreased with pressure at various temperatures is better shown in Figs. 9, 10, and 11. The curves in these figures were obtained from the data shown in the previous figure. The percentage change of the specific volume with a pressure change of 800 bars increased with the temperature and decreased with the percentage of sulfur. For instance, the specific volume of a specimen containing 3 per cent of sulfur is decreased about 3.3 per cent

at 25° C. by a pressure of 800 bars, and about 4.2 per cent at 85° C. The corresponding decreases for the specimen containing 31 per cent of sulfur are 1.8 and 2.4 per cent.

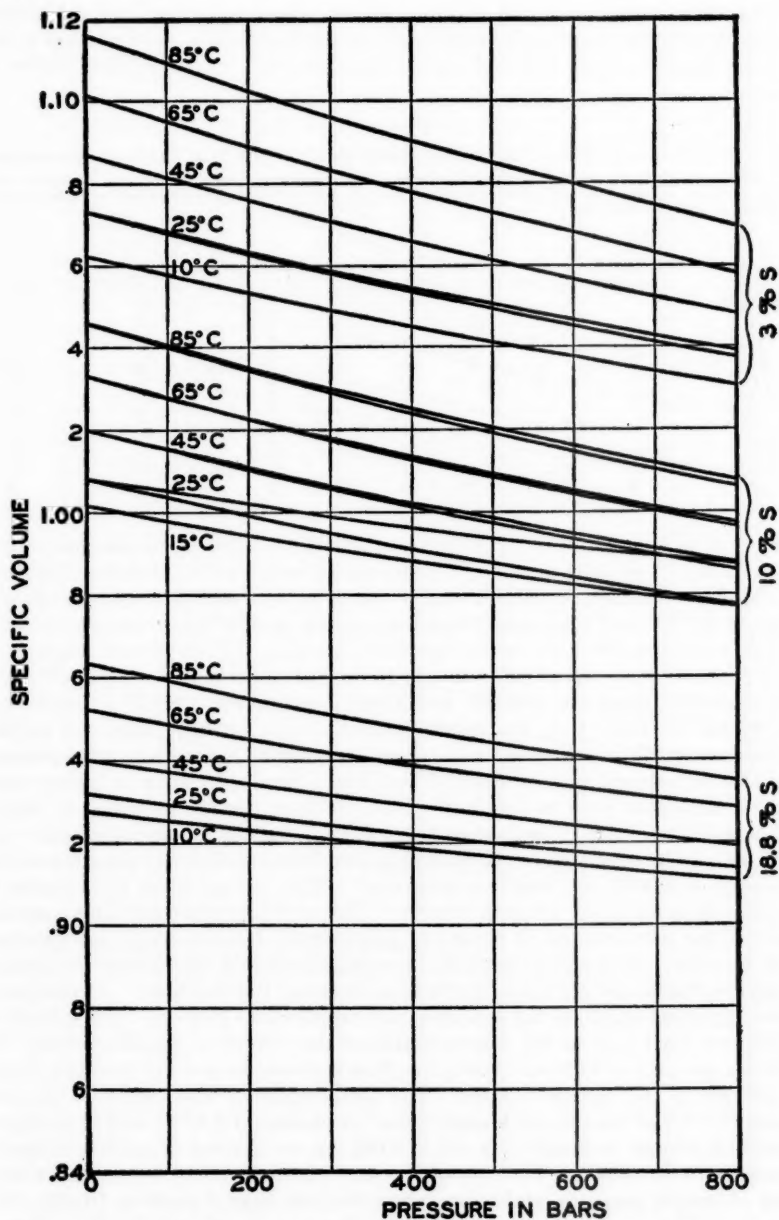


Figure 9—Effect of Pressure on the Specific Volume of Rubber-Sulfur Compounds Containing 3, 10, and 18.8 Per Cent of Sulfur

The reproducibility of the results can be seen from the spread of the points in Figs. 4 to 8, or from the curves in Figs. 9, 10, and 11. Where two curves are drawn they represent the maximum and minimum values. When more than one set of measurements was made and only one line has been drawn, the values were so close together as to be indistinguishable on the scale used. The number of sets of measurements made for each composition at each temperature is shown in Table I.

TABLE I

NUMBER OF SETS OF PRESSURE MEASUREMENTS MADE ON THE VARIOUS SPECIMENS

[A set of measurements consists of the measurements on a specimen made during one pressure cycle when pressure is increased from atmospheric pressure to 800 bars and then decreased to atmospheric pressure in steps of 200 bars.]

Sulfur Content, Per Cent	Number of Speci- mens	Number of Sets Respectively at								
		10° C.	15° C.	25° C.	35° C.	45° C.	55° C.	65° C.	75° C.	85° C.
3	1	1	..	3	..	1	..	1	..	1
6	1	2	..	4	..	2	..	2	..	1
10	2	..	1	4	2	2	..	3	..	2
11.5	2	1	..	2	..	2	..	2	..	2
16.5	1	3	..	2	..	1	..	1
18.8	1	1	..	1	1	1	..	1	..	1
19.5	1	1	..	2	1	1	1	1	..	1
25.6	1	1	..	1	..	1	1	1
31	2	..	1	5	2	3	..	4	..	3

Thus it will be seen that for 31 per cent of sulfur, 5 sets of measurements were made at 25° C. on 2 specimens. Yet the values were so close that the differences could not be shown on the figure. On the other hand, 4 sets of measurements were made at 25° C. on 2 specimens containing 10 per cent of sulfur and the values of specific volume at 800 bars varied from 0.977 to 0.987. These were extreme cases.

The variability in the results was due to lack of stability and reproducibility of the specimens, since the pressure and length measurements could be made with far greater accuracy than the results indicate. The pressure gage was capable of measuring pressure differences of $\frac{1}{2}$ bar and, during calibration, measurements could be reproduced with an error of less than 2 bars. An error of 2 bars would cause a maximum error in length of about 0.003 cm. for the specimen of highest compressibility, which is equivalent to an error in specific volume of about 1 part in 10,000. The measurement of change in length was sufficiently accurate so that a change of 0.0003 cm. could be measured. This is equivalent to a change in specific volume of about 1 part in 100,000. This probably represents the reproducibility of the measurement of change in length since the microscope and specimens were supported by separate brackets on a brick wall and the changes in pressure in the chamber could not affect the distance between the brackets. As mentioned above, the total length of the specimen was measured to 0.05 cm. Since the total length was used only in the determination of the change in specific volume with pressure, an error of 0.05 cm. in total length introduced an error of less than 3 parts in 100,000 in the specific volume. The temperature of the specimen was kept within 0.1° C. of the desired temperature. A change of 0.1° C. would produce a maximum change in length of a rod of 0.002 cm. or an error in specific volume of about 1 part in 10,000. The sum of the errors introduced by errors in measurement of length, pressure, and temperature was less than 3 parts in 10,000. The reproducibility of the measurements was therefore much greater than the reproducibility of the results.

The results on the specimens of high sulfur content were much more reproducible than those on specimens of a low sulfur content. There was some variability in the results on the specimen containing 3 per cent of sulfur, but not as much as in the results on the specimens containing from 6 to 16.5 per cent of sulfur. Instability in the properties of specimens in this range of sulfur content was noticed in previous work.

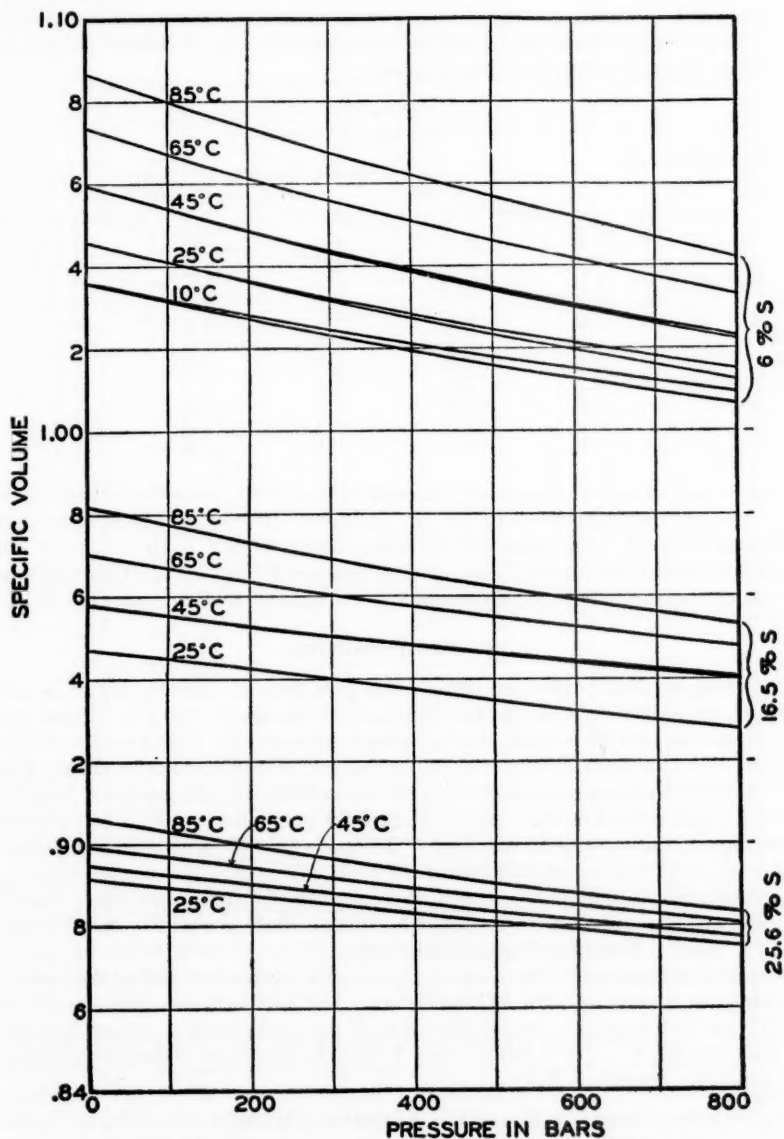


Figure 10—Effect of Pressure on the Specific Volume of Rubber-Sulfur Compounds Containing 6, 16.5, and 25.6 Per Cent of Sulfur

3. Volume Thermal Expansivity

The volume thermal expansivity as obtained from the slopes of the straight lines drawn through the points in Figs. 4 to 8 are given in Table II. The expansivities are given in two ranges of temperature for the specimens containing 18.8, 19.5, and 25.6 per cent of sulfur. The values given for these latter specimens should be considered as only approximate since they were computed for short temperature ranges, and usually only one set of measurements was made at a temperature. The values for the other specimens were computed for much larger temperature ranges and more measurements were made.

TABLE II
VOLUME THERMAL EXPANSIVITY

Sulfur Content, Per Cent	Temperature Range, ° C.	Pressure in Bars				
		1	200	400	600	800
3	10 to 85	6.7×10^{-4}	6.2×10^{-4}	5.8×10^{-4}	5.4×10^{-4}	5.0×10^{-4}
6	10 to 85	6.6	6.0	5.6	5.2	4.8
10	15 to 85	6.4	5.8	5.4	5.1	4.6
11.5	10 to 85	6.6	5.8	5.3	4.7	4.4
16.5	25 to 85	6.2	5.4	5.0	4.5	4.4
18.8	10 to 25	3.0	2.6	2.4	2.1	2.1
18.8	45 to 85	6.2	5.5	5.0	4.6	4.2
19.5	10 to 25	2.5	2.2	1.8	1.6	1.4
19.5	45 to 85	5.7	5.2	4.8	4.3	3.9
25.6	25 to 45	1.9	1.6	1.5	1.4	1.3
25.6	65 to 85	4.0	3.0	2.4	1.9	1.6
31	15 to 65	2.1	2.0	1.9	1.8	1.7

The volume thermal expansivity decreased with both pressure and sulfur content. It was decreased from 6.7×10^{-4} to 5.0×10^{-4} by 800 bars' pressure for the specimen containing 3 per cent of sulfur, and from 2.2×10^{-4} to 1.7×10^{-4} for the specimen containing 31 per cent of sulfur. Values for the latter specimen are about one-third those for the specimens containing small amounts of sulfur.

4. Compressibility

The compressibility was computed from Equation 6. The values of α and β for each set of data were computed by means of Equations 3 and 4. These coefficients and the specific volume at atmospheric pressure, V_a , were found to be functions of both the temperature and sulfur content of the specimen. From Fig. 4 it is seen that V_a increases linearly with the temperature for all specimens containing up to 16.5 per cent of sulfur. When V_a at 25° C. is plotted against the percentage of combined sulfur, it is found that it decreases linearly with the percentage of sulfur up to 16.5 per cent and from 18.8 to 31 per cent. The coefficients α and β increase with the temperature and decrease with the sulfur content. The relationship appears to be linear in each case, though there is a wide spread of values in some cases. Assuming linear relationships, it was possible to set up two sets of empirical equations for the values of V_a , α , and β , one for each side of the boundary marking the change in slope of the curves. For temperatures between 10° and 85° C. and for specimens containing up to X per cent of sulfur, where X is given by the equation $X = (T + 30)/3.7$ and T is the temperature in degrees centigrade, the following equations hold:

$$V_a = 1.1015 + 0.00073(T - 25) - X[0.00932 + 0.000007(T - 25)] \quad (7)$$

$$\alpha = -10^{-4}[53.7 + 0.258(T - 25) - X[1.35 - 0.00217(T - 25)]] \quad (8)$$

$$\beta = 10^{-9}[12.0 + 0.083(T - 25) - 0.34X] \quad (9)$$

For temperatures between 10° and 85° C. and for specimens containing between X and 32 per cent of sulfur, where X is given by the equation $X = (T + 42)/3.7$, the following equations hold:

$$V_a = 1.0450 + 0.00038(T - 25) - X[0.00601 + 0.0000064(T - 25)] \quad (10)$$

$$\alpha = -10^{-6}\{35.6 + 0.326(T - 25) - X[0.352 + 0.00672(T - 25)]\} \quad (11)$$

$$\beta = 10^{-9}[9.1 + 0.0683(T - 25) - 0.221X] \quad (12)$$

When these values of V_a , α , and β were substituted in Equation 2, equations

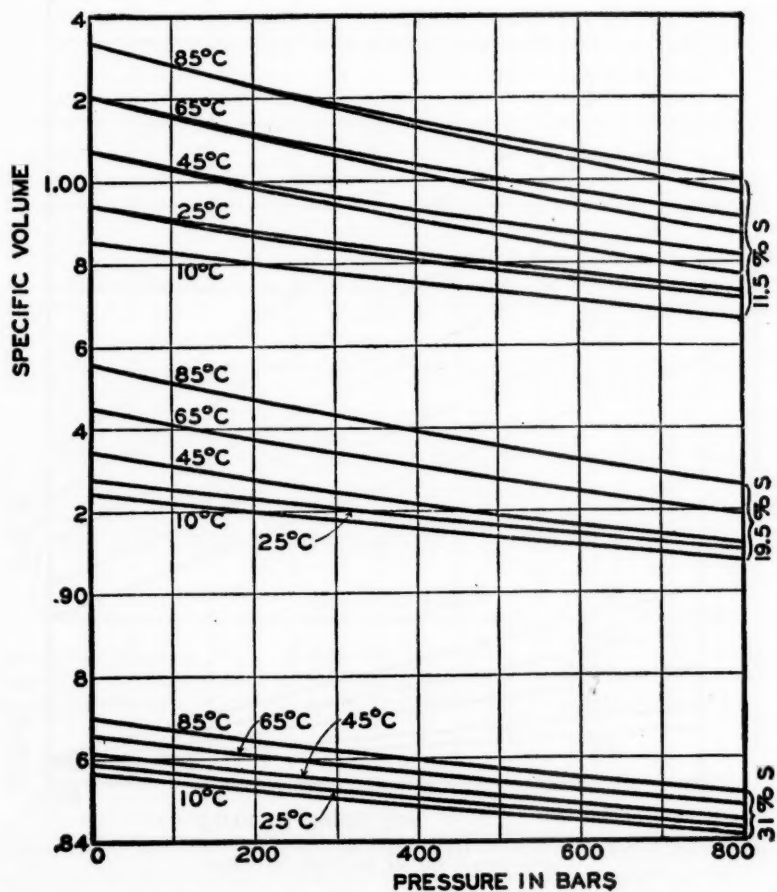


Figure 11—Effect of Pressure on the Specific Volume of Rubber-Sulfur Compounds Containing 11.5, 19.5, and 31 Per Cent of Sulfur

were obtained which gave the specific volume with an accuracy comparable to the accuracy of the data within the limits specified, with a few exceptions. The computed values of the specific volume agree to about 1 part in 1000 with experimental values for the specimens containing 3, 6, and 31 per cent of sulfur and with part of the experimental values for the specimens containing 10, 11.5, 16.5, 18.8, 19.5, and 25.6 per cent of sulfur. In one case only the computed value differs from

a measured value by more than 4 parts in 1000. The computed value for the specimen containing 25.6 per cent of sulfur at 85° C. is lower than the measured value by about 12 parts in 1000.

The values for the compressibility may be readily determined within the limits specified from Equation 6 by substituting in it the correct values of α and β as computed from Equations 8 and 9 or 11 and 12. The values for the specimens

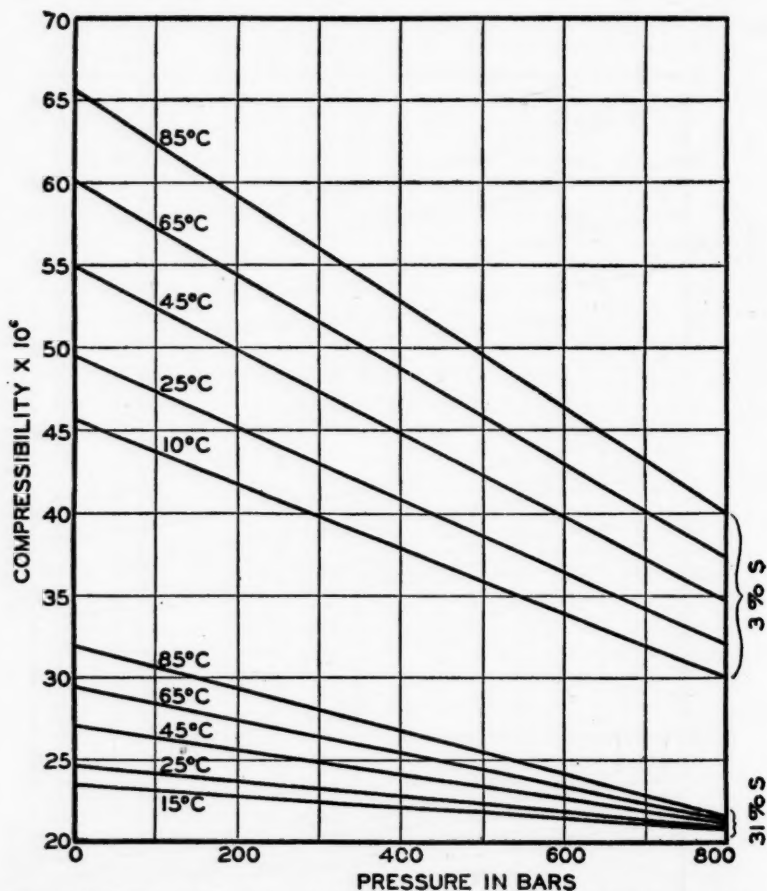


Figure 12—Effect of Pressure on the Compressibility of Rubber-Sulfur Compounds Containing 3 and 31 Per Cent of Sulfur

containing 3 and 31 per cent of sulfur are shown in Fig. 12. These were the extreme values of the compressibility which were obtained.

VI. DISCUSSION

The method used for the determinations of the specific volumes and compressibilities of rubber was such that the precision of measurement was much higher than the reproducibility of results. As mentioned above, the measurements could be made to less than 3 parts in 10,000. The reproducibility of the results was

such that during any set of measurements through a pressure cycle at a fixed temperature the values obtained for increasing pressures agreed with those for decreasing pressures to about 2 parts in 10,000. However, when a duplicate specimen was made or when the specimen was taken through a cycle of temperatures and measured again at the original temperature, the measurements in many cases did not agree closer than about 2 or 3 parts in 1000 at 800 bars. In one case the measurements on different specimens did not agree closer than 1 part in 100. The values of specific volume are therefore probably accurate to 0.2 or 0.3 per cent in most cases and in any case to 1 per cent.

There is very little published information on the compressibility of rubber with which to compare the present work. Adams and Gibson have measured 3 samples of rubber at pressures above 1000 bars.¹³ Only one of these had a composition falling in the group used in the present investigation. The extension of the curve of Adams and Gibson for a specimen containing 10 per cent of sulfur gives a compressibility of about 29.4×10^{-6} at 800 bars. The compressibility for the same composition obtained from Equation 6, using the values of α and β computed from Equations 8 and 9, is 26.4×10^{-6} at 25° C. The values obtained for the individual sets of data, where α and β were computed from Equations 3 and 4, varied from 15.5 to 29.4×10^{-6} . The value given by Adams and Gibson is then about the same as the highest value obtained by the author. But the change of the compressibility with pressure obtained by the author is very much greater than that given by the curve of Adams and Gibson.

The specific volumes of rubber-sulfur compounds at atmospheric pressure have been determined by Kimura and Namikawa.¹⁴ They used specimens made from crude rubber. The values which they reported are in agreement with those given here for specimens containing up to 16.5 per cent of sulfur. For specimens containing larger amounts of sulfur the values of specific volume given by them are lower than those given here. The "knees" which they describe were observed by the author, but they were generally found to come at lower temperatures than those reported by Kimura and Namikawa.

Acknowledgment

Acknowledgment is made of the important assistance which A. D. Cummings rendered in preparing most of the specimens used in this investigation and in helping with some of the measurements.

References

- ¹ This paper is one of a series dealing with the properties of rubber-sulfur compounds. See *Bur. Standards Tech. Paper*, **19**, 669 (1925); *Bur. Standards Sci. Paper*, **22**, 383 (1927); and *Bur. Standards J. Research*, **11**, 173 (1933). A need for information regarding the compressibility of rubber arose in connection with the determination of the effect of pressure on the electrical properties of rubber where a knowledge of the change in dimensions was required.
- ² *J. Soc. Chem. Ind., Japan*, **32** (supplemental binding) 196B (1929).
- ³ The bar is defined as 10^6 dynes/cm.² and is equal to 0.987 normal atmosphere.
- ⁴ The assumption that the samples were isotropic was based on the method of preparation, and is confirmed by recent photoelastic studies on vulcanized rubber by Thibodeau and McPherson, *J. Research Nat. Bur. Standards*, **13**, 887 (1934).
- ⁵ The cubic term in the equation which Adams and Gibson found to describe the change in volume of rubber with pressure (see *J. Wash. Acad. Sci.*, **20**, 213 (1930)) was unnecessary over the short pressure range used in the present investigation.
- ⁶ *Bur. Standards J. Research*, **11**, 243 (1933). This pycnometer is a modification of the one used by Richards, Hall, and Mair, *J. Am. Chem. Soc.*, **50**, 3308 (1928).

- ¹ *International Critical Tables*, **3**, 46.
- ² *J. Am. Chem. Soc.*, **56**, 4 (1934).
- ³ *J. Research Nat. Bur. Standards*, **13**, 617 (1934).
- ¹⁰ Scott, McPherson, and Curtis, *Bur. Standards, J. Research*, **11**, 173 (1933).
- ¹¹ *J. Soc. Chem. Ind., Japan*, **32** (supplemental binding), 196B (1929).
- ¹² *J. Research Nat. Bur. Standards*, **13**, 411 (1934), R. P. 717.
- ¹³ *J. Wash. Acad. Sci.*, **20**, 213 (1930).
- ¹⁴ *J. Soc. Chem. Ind., Japan*, **32** (supplemental binding), 196B (1929).

Refractive Index of Rubber

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I. INTRODUCTION

This paper presents an exploratory study of the refractive index of rubber.¹ Previous observations on the refractive index of rubber have been, for the most part, restricted to transparent samples. In the present investigation, however, by using reflected light rather than light at grazing incidence, it was found possible to extend the range of measurements to rubber samples that were somewhat dark in color or that were very nearly opaque. Such being the case, determinations of refractive index were made not only on translucent samples of unvulcanized or soft vulcanized rubber, but also on binary mixtures of rubber and different compounding materials, and on compounds of rubber and sulfur containing 0 to 19 per cent of sulfur and covering the range from soft to semi-hard rubber.

Different samples of unvulcanized *Hevea* rubber, of plantation origin, all showed approximately the same refractive index, irrespective of considerable variations in the nonhydrocarbon components. The index was not appreciably altered by the amount of mastication which rubber ordinarily receives in processing and mixing with compounding ingredients. Mixtures of rubber with substances insoluble in it showed the same index as the rubber itself, while mixtures with soluble substances differed in index from rubber by an amount which depended upon the index of the substance and the amount in solution. Measurements of refractive index, therefore, afford a means of measuring the solubility of substances in rubber and were employed for determinations of the solubility of sulfur and of a common antioxidant, phenyl- β -naphthylamine.

Sulfur in combination with rubber had a relatively greater effect on the refractive index than did sulfur in solution. For vulcanized rubber-sulfur compounds in the soft-rubber range, the refractive index was a simple linear function of the percentage of sulfur and also of the temperature. Preliminary measurements on vulcanized compounds in the hard-rubber range indicate that the change in physical properties of rubber-sulfur compounds from soft to hard was accompanied by a decrease in the slope of the curve relating refractive index to temperature.

II. METHOD OF MEASURING REFRACTIVE INDEX OF RUBBER

The measurements of refractive index were made on critical-angle refractometers of the Abbé type, but the border-line characteristic of rubber was obtained by using reflected light rather than light at grazing incidence. Two instruments were used. One was designed for this type of measurement, but it had the practical limitation that the prism was not jacketed to permit the circulation of water for temperature control. This instrument was used in a constant-temperature room at approximately 25° C. In order to make observations over a range of temperature a standard Abbé refractometer having a water-jacketed prism was employed. Since there was no provision for admitting light into the prism from the face opposite the one on which the specimen was mounted, a slab of plane-parallel glass having ground edges was interposed between the specimen and the prism. Light was introduced through the edge of this slab, as illustrated in Fig. 1.

The illuminating prism was, of course, removed. The specimen and glass slab were enclosed on three sides by a cored metal housing. The control of temperature was secured by circulating water through this housing and the jacket around the prism. The glass slab had a refractive index of 1.65, which was significantly higher than that of the rubber, as required by the optical system. α -Bromonaphthalene was employed to obtain optical contact between the glass slab and the prism.

Samples of rubber for measurement were mounted on the prism of the refractometer or on the glass slab without employing a contact liquid. No difficulty was experienced in obtaining good optical contact between soft rubber and glass, provided the surface of the rubber was clean and smooth. This condition was met

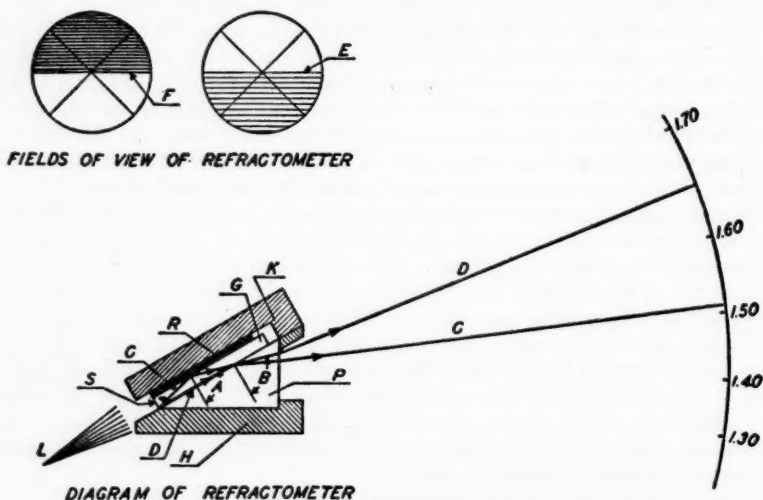


Figure 1—Optical System for the Measurement of Refractive Index

R, rubber sample; G, plane parallel glass slab with fine ground edge toward light source; P, refractometer prism; L, light source; A, critical angle characteristic of rubber; B, critical angle characteristic of glass slab; C, limiting emergent ray for rubber; D, limiting emergent ray for glass slab; E, critical edge or border line characteristic of rubber; F, critical edge or border line characteristic of glass slab; H, metal housing cored for circulation of water.

by molding the specimens between sheets of polished aluminum, and by removing the aluminum just before the rubber was to be attached to the glass. In preparing crude-rubber specimens, the rubber was milled until it ran smoothly on the rolls, compounding ingredients, if any, were added quickly, and the resultant batch was pressed out between thin aluminum sheets in a vulcanizing press at about 100° C. Vulcanized specimens were cured between the aluminum sheets.

Samples of hard or semi-hard rubber did not give good contact when pressed against glass at room temperature. These were prepared in sheets about 0.25 mm. in thickness and were mounted on the glass slabs by pressing them together hot and allowing them to cool under pressure.

When measurements of refractive index are made by the method here employed the contrast between the two halves of the field, seen in the telescope of the refractometer, is not great. This contrast is diminished as the samples become darker in color or increase in opacity, and the boundary often becomes less distinct.

This constitutes a limitation of the method, both as to the range of samples that can be employed and as to the precision of measurement.

III. REFRACTIVE INDEX OF UNVULCANIZED RUBBER

Several different samples of unvulcanized rubber, of plantation *Hevea* origin, were examined, and all were found to possess approximately the same refractive index, irrespective of their hydrocarbon content or method of preparation. This is shown by the results given in Table I. Two samples of rubber obtained by the evaporation of ammonia-preserved latex from different sources gave indices, n_D^{25} , of 1.5187 and 1.5192, respectively. Different samples of commercial smoked sheet and pale crepe gave indices from 1.5187 to 1.5189, with an average of 1.5188, while for purified rubber the index ranged from 1.5189 to 1.5191, with an average of 1.5190.² The various samples of unvulcanized rubber differed materially in composition and in the treatment which they were accorded in preparation. The latex rubber contained about 10 per cent of resins, proteins, and soluble serum components, while the purified rubber contained about 0.5 per cent of non-hydrocarbon components. The smoked sheet and pale crepe contained intermediate but not identical amounts of nonhydrocarbon components. The rubber from latex was given no mechanical or heat treatment, while the purified rubber was subjected to prolonged mastication and a high temperature in the purification process.

Two reasons may be suggested for the uniformity in refractive index of different samples of rubber. In the first place, the non-hydrocarbon components such as the proteins, which are insoluble in the rubber, have no effect on the index, because the hydrocarbon is the external or continuous phase and produces the refraction at the rubber-glass interface. In the second place, the soluble components, such as the resins, have only a relatively slight effect on the refractive index, because they possess approximately the same index as rubber.

As was noted in the previous section, the samples of crude rubber were prepared for measurement by milling them for a short time, after which they were pressed between sheets of aluminum. In order to determine the effect of mastication, samples of smoked sheet rubber were milled for intervals from 5 to 30 minutes and measurements of the index made. The results, which are shown in Table I, indicate that there was no progressive change in the refractive index with the time of milling, so it was concluded that this step in the preparation of the samples, as it was conducted in the present investigation, was without significant effect on the index.

TABLE I
REFRACTIVE INDEX OF UNVULCANIZED RUBBER

Kind of Rubber	Sample No.	Treatment of Sample	n_D^{25}
Film from evaporation of latex	1	None	1.5187
	2	None	1.5192
Pale crepe	1	Milled	1.5187
	2	Milled	1.5188
	3	Milled	1.5187
Smoked sheet	1	Milled	1.5188
	2	Milled 5 min.	1.5188
	2	Milled 10 min.	1.5188
	2	Milled 20 min.	1.5189
	2	Milled 30 min.	1.5188
Purified	1	(^a)	1.5191
	2	(^a)	1.5190
	3	(^a)	1.5190
	4	(^a)	1.5189

^a See *Bur. Standards J. Research*, 11, 175 (1933).

In addition to the studies on plantation rubber, refractive-index measurements were made on twenty samples of representative types of wild rubber, which were kindly furnished by the U. S. Bureau of Plant Industry, Office of Cotton, Rubber, and Other Tropical Plants. The samples ranged in index, n_D^{25} , from 1.5191 to 1.5242, with an average value of 1.5208. The results are not here reported in detail because no study was made to correlate the indices of the various samples with their composition, or to ascertain the indices of the hydrocarbon fractions in the pure state.

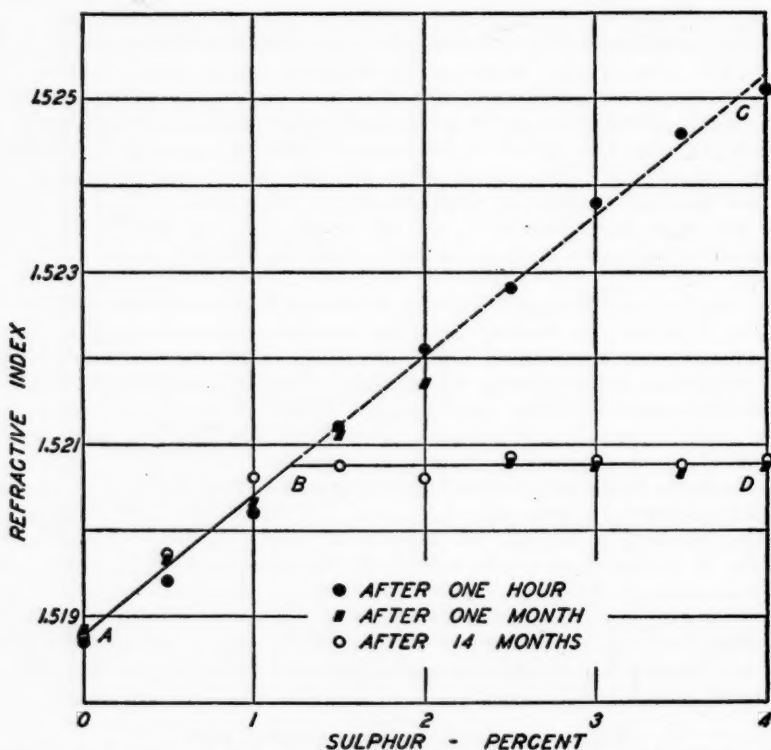


Figure 2—Refractive Index of Rubber-Sulfur Mixtures at Different Times after Mixing
AB represents unsaturated solutions of sulfur in rubber; BC, supersaturated solutions; and BD, a saturated solution.

All of the above measurements of refractive index relate to the D line of the spectrum. One sample of purified rubber, however, was measured on a Pulfrich refractometer with light of two other wave-lengths, and the following results were obtained:

Line	Wave-Length in Angströms	Refractive Index
C (H_α)	6563	1.5153
D	5893	1.5190
F (H_β)	4861	1.5483

The dispersion, $H_\alpha - H_\beta$, was therefore 0.0330.

IV. REFRACTIVE INDEX OF MIXTURES OF UNVULCANIZED RUBBER WITH COMPOUNDING MATERIALS

1. Rubber-Filler Mixtures

Measurements of the refractive index were made on samples of crude rubber mixed with different proportions of whiting, zinc oxide, barytes, titanium dioxide, carbon black, and zinc stearate. Only in the case of zinc oxide was there any significant difference between the index of the mixtures and that of the rubber. A freshly prepared mixture of pale crepe, $n_D^{25} = 1.5188$, with 4 per cent of "Kadox" zinc oxide, showed an index of 1.5220. A mixture of the same rubber with 4 per cent of "XX-Red" zinc oxide, however, had an index of 1.5209. With smaller percentages of the two oxides, lower values of the index were obtained. It is probable that some zinc oxide reacted with nonhydrocarbon constituents of the rubber to form salts which dissolved in the rubber and changed the index. A definite statement, however, cannot be made without further experimental work.

As was mentioned previously, the addition of filler to rubber increased the difficulty of reading the refractive index by reducing the contrast between the two halves of the field and by rendering the boundary between them less sharp. With carbon black satisfactory observations were obtained for mixtures containing not more than 0.1 per cent. With titanium dioxide the amount was of the order of 2 per cent. In the case of zinc stearate, however, fairly satisfactory observations were made on stocks containing as high as 50 per cent.

2. Rubber-Sulfur Mixtures

When rubber was mixed with sulfur on the mill in proportions up to 4 per cent, it was possible to cool the resulting stocks to 25° C. and measure the index before any separation of the sulfur or blooming took place. For such stocks the index was a linear function of the percentage of sulfur, as is indicated by the curve ABC in Fig. 2. This curve relates to solutions of sulfur in crude rubber and is described by the equation,

$$n_D^{25} = 1.5188 + 0.0016S,$$

where S is the percentage by weight of dissolved sulfur.

When these stocks were permitted to stand, sulfur separated from those in which it was present in larger amounts, and the index decreased. The measurements after 1 month and 14 months are shown in the figure. At the end of 1 month the index of the samples containing from 2.5 to 4.0 per cent of sulfur had dropped to the constant value 1.5208, while the index of the samples containing 2.0 per cent had dropped a little, and that of the samples containing 1.5 per cent was practically unchanged. After 14 months, however, the indices of these last two compositions had dropped to about 1.5208, while those of the other compositions remained practically unchanged. This indicates that the value 1.5208 is the refractive index of a saturated solution of sulfur in rubber at the temperature of the room in which the samples were stored, which was approximately 25° C. As may be seen from the curve, this index corresponds to a solubility of about 1.2 per cent. This is somewhat higher than the value 0.85 per cent which is obtained by extrapolation from measurements of the solubility of sulfur in rubber by Morris.³

3. Mixtures of Rubber and Phenyl- β -Naphthylamine

Measurements of the refractive index were made on samples which contained from 1 to 8 per cent of phenyl- β -naphthylamine, and yielded results quite similar

to those obtained with the rubber-sulfur stocks. The index of the freshly prepared stocks in which no crystallization had taken place is given by the equation,

$$n_D^{25} = 1.5188 + 0.0015P$$

where P is the percentage of phenyl- β -naphthylamine. This equation agrees with the observations with a maximum deviation of 0.0003 and an average deviation of 0.0001. When the samples were remeasured after 14 months, those which had contained from 2 to 8 per cent of the solute all showed values of n_D^{25} , between 1.5204 and 1.5208, with an average of 1.5206. Taking this as the index of a saturated solution, the solubility of phenyl- β -naphthylamine in rubber is about

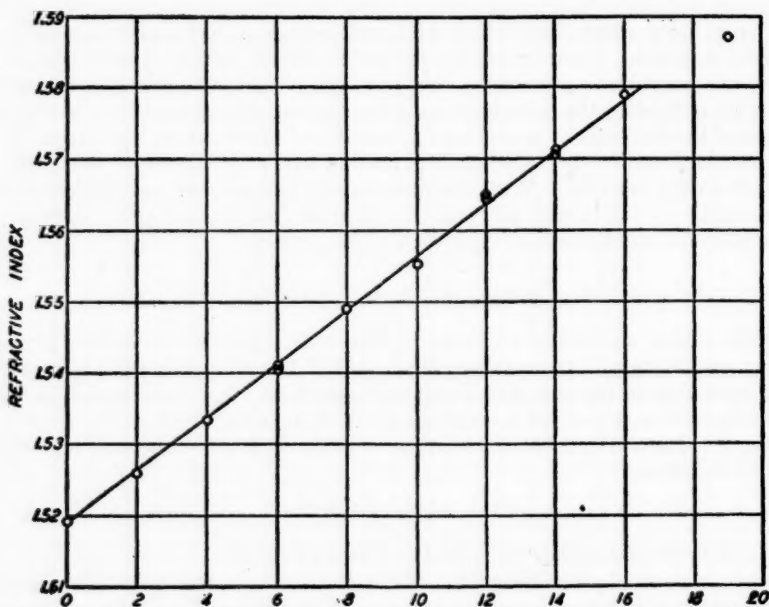


Figure 3—Relation of Refractive Index of Rubber-Sulfur Compounds at 25° C. to Percentage of Combined Sulfur

1.2 per cent. By extrapolation from the measurements by Morris, referred to above, the value 0.7 per cent was obtained.

V. REFRACTIVE INDEX OF VULCANIZED RUBBER

Measurements of refractive index were made on vulcanized rubber to determine the relation of the index to the percentage of combined sulfur and the temperature. The samples used were prepared from purified rubber and sulfur in connection with an investigation of the electrical properties.⁴ The conditions of vulcanization were such that very nearly all of the sulfur was brought into combination with the rubber. The range of composition on which measurements are here reported extends from 0 to 19 per cent of sulfur, or from unvulcanized rubber to semi-hard rubber. The effect of temperature was investigated for some of the samples, and the range covered was from about 10° to 75° C.

1. Effect of Combined Sulfur at 25° C.

The refractive indices of rubber-sulfur compounds are presented graphically in Fig. 3, in which the index is plotted against the percentage of combined sulfur. The index bears a linear relation to the sulfur content up to 16 per cent. The only higher point shown is at 19 per cent of sulfur and falls below the line for a reason

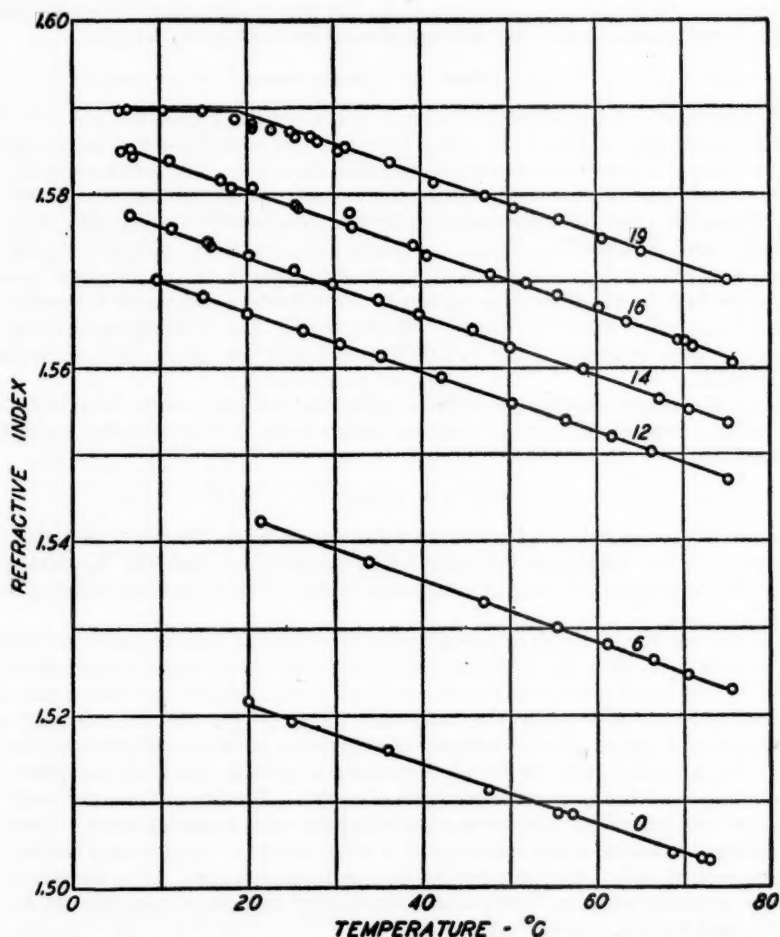


Figure 4—Relation of Refractive Index of Rubber-Sulfur Compounds to Temperature
The figures on the different curves denote the percentages of combined sulfur.

which will be discussed in the next section of this paper. Few of the measurements were made at exactly 25° C. In some instances the refractive indices at 25° C. were read from a curve which related the indices to temperature. Most of the measurements, however, were made at temperatures which differed from 25° by only 1° or 2° C., and were reduced to this standard temperature by the use of the temperature coefficient discussed in a later paragraph. The relation shown in

Fig. 3 between the refractive index at 25° C. and the percentage of sulfur is described by the equation,

$$n_D^{25} = 1.5190 + 0.00370S_c$$

where S_c is the combined sulfur expressed in percentage. In a report⁵ describing preliminary measurements the index was expressed as a linear function of the sulfur content in terms of atoms of sulfur per C_6H_8 , but the present results indicate a more nearly linear relation when the sulfur is given in percentage by weight.

2. Effect of Temperature

Measurements of the refractive index of rubber-sulfur compounds are also presented graphically in Fig. 4, in which they are plotted against the temperature. In the range of temperature under consideration the index of the samples containing from 0 to 16 per cent of sulfur decreased linearly with increasing temperature. The change in index per degree centigrade was from 0.000345 to 0.00036, with an average value of 0.00035. This is in reasonable agreement with the change in index, 0.00036 per degree centigrade, reported in a previous investigation by one of the authors.⁶ Kirchhof⁷ has measured the refractive indices of a number of samples of crude rubber at different temperatures. His observations indicate a change in index of from 0.00034 to 0.00042 per degree centigrade, with an average of 0.00039.

When the relation between refractive index and temperature is combined with the relation between refractive index and sulfur content, the following expression is obtained,

$$n_D^{25} = 1.5190 + 0.00370S_c - 0.00035(t - 25)$$

where S_c is the percentage of combined sulfur, and t is the temperature in degrees centigrade. The maximum deviation of observations at different temperatures from values computed by this equation was 0.0015 and the average deviation was 0.0006.

The curve in Fig. 4, which relates the refractive index of the compound containing 19 per cent of sulfur to the temperature, shows a change in slope at approximately 17° C. This point represents the intersection of two straight lines drawn through the points above and below the transition, respectively. As indicated by the observations, however, the transition is not sharp but gradual, and this is probably the reason why the index at 25° C. does not fall quite in line with the indices of compounds containing lower percentages of sulfur. The transition is probably of the type designated by Ehrenfest as a transition of the second order.⁸ Such a transition is indicated in the same region of temperature for a compound containing 19 per cent of sulfur, by temperature-volume measurements. The temperature-volume measurements by Kimura and Namikawa⁹ indicate a transition at about 30° C., and those by Scott,¹⁰ at about 34° C.

Some preliminary measurements of the refractive indices of other rubber-sulfur compounds have been made in the range of composition from 19 to 32 per cent of sulfur. These indicate transitions similar to the one observed for the 19 per cent compounds.

3. Change of Refractive Index during Vulcanization

The combination of a given quantity of sulfur with rubber increases the refractive index more than the solution of the same quantity of sulfur in the rubber, consequently when a rubber stock is vulcanized there is a progressive increase in

refractive index until all of the sulfur is brought into combination. Measurements of the index were made on several practical rubber compounds during vulcanization. There was a progressive increase in index, but the magnitude was not precisely that predicted from the amount of sulfur which went into combination with the rubber, probably because reactions of accelerators and zinc oxide accompanied the addition of sulfur and changed the index of the product.

Acknowledgment

The authors are grateful to L. W. Tilton and J. K. Taylor of this Bureau for advice and assistance in connection with the measurement of refractive indices.

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¹ A preliminary report on this subject, entitled "Effect of Vulcanisation on the Refractive Index of Rubber," was published in the Technical News Bulletin of the Bureau of Standards, No. 194, page 66, June, 1933. This report was published, with comments by F. Kirchhof, in *Kautschuk*, Vol. 9, No. 11, page 172, November, 1933, where the original source of publication was not mentioned. The *Kautschuk* article was in turn printed in RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 7, pages 608-9, October, 1934. Other publications on the refractive index of rubber are: Ayrton and Perry (and Jellett), *Phil. Mag.*, [5], **12**, 196 (1881); Gladstone and Hibbert, *J. Chem. Soc. Trans.*, **53**, 680 (1888); Curtis and McPherson, *Tech. Pap. Bur. Standards*, **19**, 698 (1925); Tanaka, *Trans. Inst. Rubber Ind.*, **2**, 330 (1927); and Shacklock, *Ibid.*, **7**, 354 (1932); Kirchhof, *Kautschuk*, **8**, 137-42 (1932); RUBBER CHEM. AND TECH., **6**, 92 (1933).

² This value is a little higher than the value $n_D^{25} = 1.5184$ previously reported by one of the authors, *Bur. Standards J. Research*, **8**, 756 (1932).

³ *Ind. Eng. Chem.*, **24**, 584 (1932).

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⁵ *Bur. Standards Tech. News Bull.*, **194**, p. 66 (June, 1933).

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⁷ *Kautschuk*, **8**, 137 (1932); also RUBBER CHEM. AND TECH., **6**, 92 (1933).

⁸ See Bekkedahl, *J. Research Natl. Bur. Standards*, **13**, 424 (1934), R. P. 717.

⁹ *J. Soc. Chem. Ind., Japan*, **32** (supplemental binding), 196B (1929).

¹⁰ Arnold H. Scott, *J. Research Natl. Bur. Standards*, **14**, 99 (1935), R. P. 760.

Synthetic Rubber. Its Industrial Production in the U. S. S. R.

I. G. Akobzhanov

The subject of synthetic rubber has not been neglected in the literature. However, all the publications, including those of Harries¹ or some of the work of Dubosc and Luttringer² or even the less complete works such as articles by Jacobs³ and by Whitby and Katz,⁴ contain systematic discussions of the various possibilities of synthesizing rubber, but these deal only with established laboratory procedures, which are for the most part theoretical for the very reason that they have been merely abstract researches and have not been applied on an industrial scale.

It should, however, be mentioned that the recent publications of Carothers and his collaborators⁵ are not of this character, and Gottlob,⁶ who described the great efforts in the Beyer and Co. plant at Leverkusen where 200 tons per month of synthetic rubber were produced during the war, should likewise not be overlooked. Nevertheless a description of this latter process is not of much practical value, because it deals with a process which was abandoned a long time ago. As far as any interest today in the industrial synthesis of rubber is concerned, there is only the work being carried out in U. S. S. R.

The author would refer economists and rubber technologists who may be interested in the details to his earlier article,⁷ and the purpose of the present article is limited to a detailed survey of the chemical process as applied in the U. S. S. R., leaving out of consideration an analysis of the reasons why it has been considered necessary in the U. S. S. R. to carry out this undertaking, and why ethyl alcohol has been adopted as a raw material for the synthesis of the new rubber, and leaving out of consideration all the statistics of the development of this industry and also technical information for the use of this new substance in rubber factories.

In order for a substance to be termed rubber, whether natural or synthetic, it must possess the following two characteristics:

1. A plasticity which makes possible the incorporation of mineral and other fillers necessary for the subsequent use of the mixture, and which likewise makes it possible to give the mixture any form desired.

2. The ability to vulcanize, which transforms the plasticity into elasticity so that the form of the vulcanized object is preserved permanently.

In the U. S. S. R., four substances which can be said to meet these requirements are receiving attention:

Sovprene, which is a product of the polymerization of β -monochlorobutadiene, $H_2C:CClCH:CH_2$, and is analogous to Duprene which E. I. du Pont de Nemours and Company in the United States synthesized for the first time.

Thiokol (formerly called Resinit), which is a product of the reaction of ethylene and sodium polysulfide:



SKA and *SKB*, both of which are polymers of butadiene.

We shall discuss *SKB*, because the work with the other three has not yet passed

the experimental stage, whereas SKB has already been used in the manufacture of pneumatic tires, footwear, etc.

Unlike SKA, which is produced from butadiene with a petroleum base, SKB (the initials mean synthetic rubber manufactured according to process B) is made from butadiene with ethyl alcohol as the raw material.

Ostromislenski,⁸ in 1915, developed a synthesis of butadiene (biviny) in the following way:



However, this process is not used in the U. S. S. R. because Professor Lebedev has developed a simpler one.⁹

The Manufacture of Butadiene

British patent 331,482 of December 6, 1930, describes this process in the following way.

Methyl, ethyl, and propyl alcohols, either absolute or containing water, as well as a mixture of these alcohols, are treated with dehydrating and dehydrogenating agents, *i. e.*, uranium oxide, hydrosilicates, aluminum oxide, oxides and salts of zinc, manganese, etc.

Figure 1 shows the original column of Professor Lebedev. This is an oven consisting of a tube (11) of pure copper (or preferably of enameled sheet iron) 120 centimeters long and 10 centimeters in diameter, closed by means of two discs.

Through the lower disc is passed a pure copper tube (6) 3 centimeters in diameter which is closed at one end. The catalyst is introduced into the space between the walls of the two tubes. Heating is carried out by a nickel-chrome wire (8) wound around the outside tube, and the inner tube is equipped in a similar way. The superheated alcohol vapors enter through opening (9). (1) and (7) on the diagram are thermocouples.

The products of the reaction are immediately cooled to 0° C. The alcohol that has not reacted and various other products are condensed, while the gases carry off most of the butadiene.

In the columns a counter-current of oil of turpentine, petroleum, or alcohol, at 0° C. removes the butadiene from these gases, which are then drawn into a gasometer.

The butadiene which is distilled from the liquid in the columns is condensed by cooling or by compression. It is washed with water to remove the acetaldehyde formed, and is then rectified.

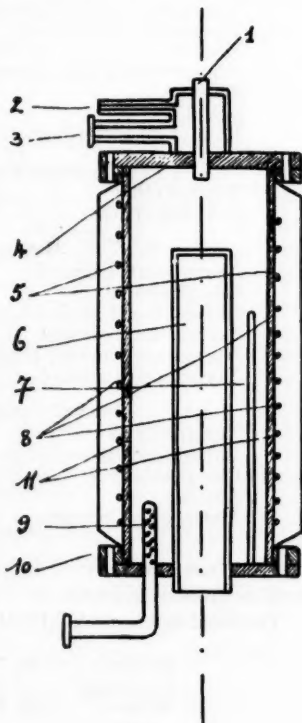


Figure 1

This butadiene, which distills between -5°C . and 2°C . has the following composition:

Butadiene, 75-80%
Pseudo-butylene, 20-15%
Ethers containing 5 carbon atoms and other ethers, up to 5%.

The pressure used in this process is approximately atmospheric pressure. In order to avoid the formation of polymers, the temperature is maintained at $400-450^{\circ}\text{C}$.

Based on the results of a large number of experiments, one is justified in regarding butadiene (or biviny) as one of the most common forms into which hydrocarbon

TABLE I

Product	Per Cent
Hydrogen	1.3-1.6
Carbon monoxide	0.2-0.5
Hydrocarbons	
Methane and other saturated hydrocarbons	0.4-0.6
Ethylene	5-8
Butylene (2-butene)	3-4
Biviny	20-25
Symmetric methylethylethylene (2-pentene)	0.5-0.7
Pipenylene (2-pentene)	0.5-0.7
Hexene	0.4-0.5
Bipropenyl (2,4-hexadiene)	0.6-0.8
Toluene	0.1-0.2
p-Xylene	0.5-0.7
Biviny dimer (ethinyl-1-cyclohexene-3)	approx. 0.05
Simple Ethers	
Diethyl ether	2-5
Ethylbutyl ether	0.5-1
Alcohols	
Normal butyl alcohol	2-4
Crotyl alcohol	0.5-1
Normal hexyl alcohol	0.5-0.8
Normal amyl alcohol	approx. 0.1
Normal unsaturated hexyl alcohol	0.05-0.1
Normal octyl alcohol	approx. 0.3
Carbonyl Compounds	
Acetaldehyde	2.5-5
Butyric aldehyde	0.1-0.2
Crotyl aldehyde	approx. 0.05
Acetone	0.3-0.5
Methylethyl ketone	0.1-0.2

residues are transformed in pyrogenic reactions. (It is formed from mazout as well as from ethylene.)

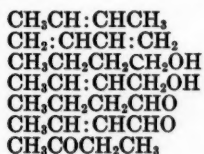
The ideal reaction: $2\text{C}_2\text{H}_5\text{OH} \rightarrow 2\text{H}_2\text{O} + \text{H}_2 + \text{H}_2\text{C}:\text{CHCH}:\text{CH}_2$, would yield:

Biviny	58.7%
Hydrogen	2.2%
Water	39.1%

In reality the various products shown in Table I were obtained. This is for a catalyst composed of 75 per cent of dehydrating agent and 25 per cent of dehydrogenating agent.

Most of the products of this reaction can be classified into groups having a common structure of 4, 6, and 8 atoms of carbon.

For example, there are for C_4 :



The formation of other products with even numbers of carbon atoms is not difficult to explain. On the other hand, there is no undisputed explanation for

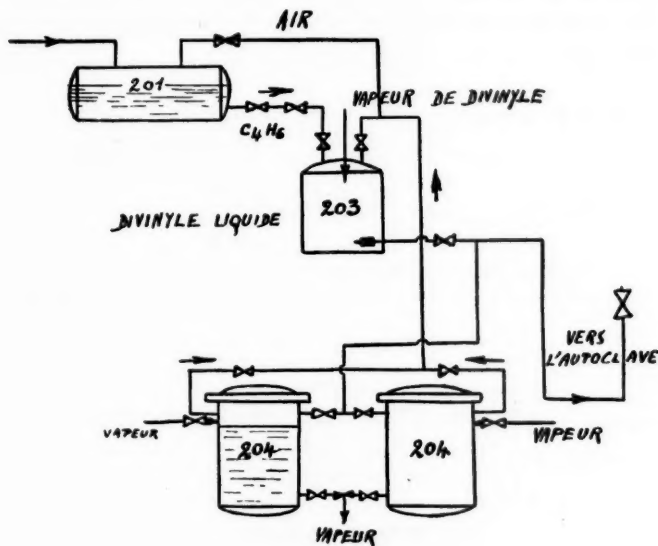
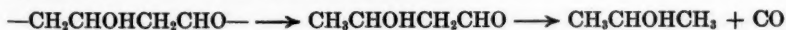


Figure 2

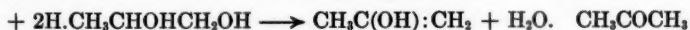
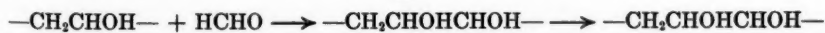
those having odd numbers. It is certain, however, that the primary cause is to be found in the loss of pairs of molecules (probably aldehydes):



For the group with three carbon atoms (acetone and propylene are found among the products of the reaction) there would be:



or



or perhaps

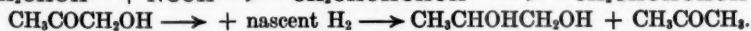
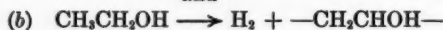
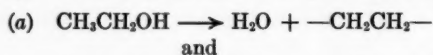


TABLE II

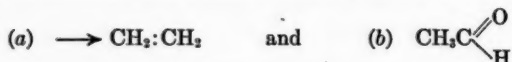
No. of Experiment	Concentration of Bivinyll	Plasticity of the Polymer
129	21.40	Flows—liquid
165	46.00	0.91
680	65.10	0.76
1213	79.20	0.60

The conditions of this reaction make possible the hydrogenation of open chains as well as additions of hydrogen, whereas derivatives of benzene can only add hydrogen.

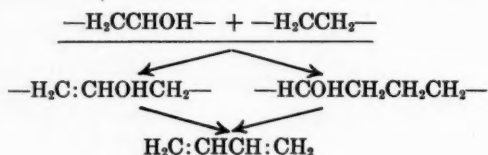
The reactions involving the formation of ethylene, of acetaldehyde and of bivinyll are closely related. Bivinyll, however, does not form molecules of the already stabilized ethylene and of the aldehyde, because a mixture of these two products when made to react in the presence of a catalyst gave only traces of bivinyll. The reaction must take place between the residues fixed by the catalyst.



If the residues lose contact with the catalyst there is obtained:



However, in order to judge the reaction by the quantity of the products which are formed, another reaction leading to bivinyll is more easily carried out:



Polymerization¹⁰

Polymerization is the subject which has been least investigated in the synthesis of rubber. At the present time the following apparatus is used in the U. S. S. R. (Factory No. 1 at Iaroslavl). (See Fig. 2.)

In Fig. 2, 201 is a reservoir for bivinyll, 203 a calibrated vessel for measuring it, and 204 (two) are receptacles for the bivinyll recovered.

By utilizing the vapor pressure of bivinyll in these two receptacles 204, as it comes from the repolymerized residues which are recovered by saving the vapors from the autoclaves (air under pressure cannot be used because of the danger of explosive mixtures), the bivinyll is passed from vessel 203 into the autoclave for polymerization.

This autoclave is a vertical heater with a double jacket, which permits heating with steam and cooling to -15°C . with water or cooling solution. The actual vessel for the polymerization is a cylindrical enameled sheet iron chamber, 3 millimeters thick, which is placed inside the autoclave.

The manufacture of the catalyst is the first step in the process of polymerization. The catalyst is in the form of a seventy-two tooth comb (teeth in rows of 12 by 6), made of iron wire, which receives the following treatment:

After the removal of the last residue of SKB (from a previous polymerization), the comb is immersed in a bath of hot 10–20 per cent hydrochloric acid or sulfuric acid. This cleaning lasts for one hour, and is followed by careful washing with water.

After testing with litmus for the absence of traces of acids, the comb is dried. Once dried and traces of surface oxidation removed, the comb is immersed in fused metallic sodium to a depth of 95 to 110 centimeters. One-half per cent of sodium based on the technical bivinyl used is necessary. The layer of sodium is then covered with a layer of paraffin (about 0.7 per cent of paraffin based on the technical bivinyl).

On the rim of the reaction vessel, which has been placed in the autoclave, is an iron ring to support the catalytic comb which is immersed in the vessel. The

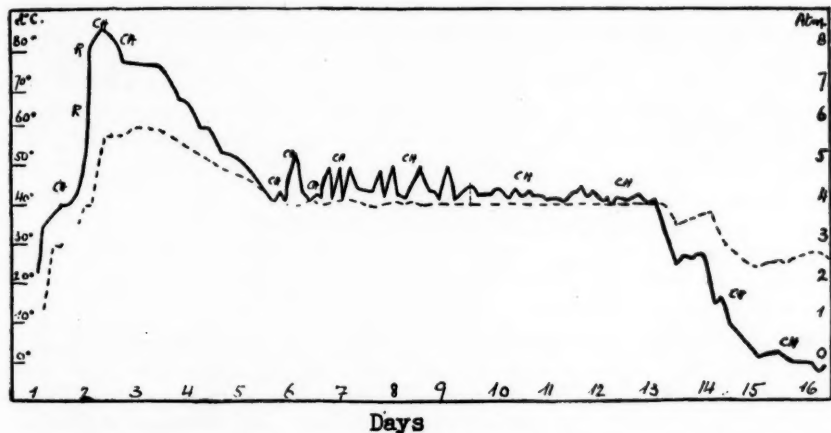


Figure 3

— Pressure (Atm.)
 --- Temperature

CH Heating
 R Cooling

comb is placed in position, and a tight seal is assured by testing under compressed air at a pressure of 8 atmospheres (the air must be thoroughly dry because of the sodium). The next step is then to fill the vessel. The quantity of technical bivinyl which gives an optimum yield, *viz.*, 83.4 per cent, is 1700 liters.

Figure 3 shows the thermal conditions of the process for a typical polymerization.

By opening and closing the steam valves, the filled autoclave is heated to 30° C., at which temperature the reaction begins. This temperature must be reached fairly rapidly. It is necessary, however, not to exceed 5 atmospheres' pressure in the autoclave. An hour will be required after the last heating at 30° C. for the reaction to commence, although there have been cases of reactions that began before 30° C.

Since the polymerization reaction is exothermic, *viz.*, 34 gram-calories per kilogram of rubber, there is a spontaneous rise in temperature, which becomes rather energetic after 6 to 8 hours, and requires cooling with water or a cooling solution. While polymerization is going on (90 to 120 hours), the temperature should be kept around 65° C. and the pressure at 8 atmospheres. A good yield is dependent upon careful cooling. However, one of the greatest dangers is premature cooling,

which "gels" the reaction in such a way that later it proceeds only very slowly, and requires several months for complete polymerization.

Toward the end of the reaction, the temperature drops to 40° C. A sample of gas from the interior is taken, and the reaction is considered satisfactory if this gas contains not over 10 per cent of bivinyl. This temperature of 40° C. is maintained for 3 to 8 days, which is the time required for "ripening." In some cases "ripening" continues from 10 to 12 days, and here again an analysis of the gas will indicate this. This longer time of "ripening" does not influence the quality of the polymerization product. The quality is judged by a plasticity test, measured according to the Karrer method. It should not exceed 0.7, and depends among other things upon the concentration of bivinyl in the technical product (see Table II), and also upon the structure of the catalyst.

The most suitable concentration is from 74 to 75 per cent of bivinyl. If the residue from the distillation of technical bivinyl is in the neighborhood of 1 per cent, there is the likelihood of not obtaining a satisfactory polymer. The content of acetaldehyde should not exceed 0.05 per cent. This low content is attained by washing the technical bivinyl with water, and since the presence of water is very dangerous on account of the catalyst, it is necessary to use great care in the process.

Since the work was begun, a change in the time of polymerization has been found to take place. Thus in 1933, there were required for

May	15.9 days
June	18.6 days
July	21.6 days
August	19.7 days
September	13.6 days
October	11.5 days

We have already mentioned the fact that pneumatic tires are being manufactured with SKB. Last summer an automobile equipped with tires made from natural and synthetic rubber made a trip from Moscow to Kara-Komo in Turkestan and back to Moscow. The mileage of the synthetic tires averaged 10,000 kilometers. It is reasonable to think that this result, good as it is, can be improved. In this connection, attempts are now being made to produce polymers with plasticities equal to 0.5 and 0.4.

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Influence of the Gaseous Medium on Hot Vulcanization

B. V. Buizov and M. K. Popova

The results of our previous study of the thermal vulcanization of rubber made it sufficiently clear that during the heating of rubber mixed with sulfur two complex phenomena take place. On the one hand, sulfur interacts with rubber, and on the other, rubber itself undergoes a depolymerization, as well as a polymerization. In reality, however, vulcanization does not proceed under ideal conditions. The rubber and sulfur in the mixture cannot be conceived in an isolated state. On the one hand, the mixture contains the accompanying substances of rubber, such as resins, albumin, etc., whose role in the vulcanization is far from being explained, and on the other hand, the system: rubber + sulfur always exists in some medium. The latter may be either a gaseous or a liquid medium. Hot vulcanization in the industry is most frequently performed in an atmosphere of hot air or in water vapor. We know how great is the difference in the effects of these two conditions. To be sure, the pressure under which the vulcanization takes place is also of importance here; however, the nature of the gaseous medium has evidently a considerable influence on the vulcanization process, which has never been investigated. It seemed to us therefore of interest to investigate this problem, considering the above mentioned two factors, *i. e.*, chemical binding of sulfur and physical changes in the rubber. The previous investigation had shown that the chemical binding of sulfur alone does not explain the nature of vulcanization. Thus, in some cases rubber on heating combines with sulfur, but at the same time disintegrates into a sticky mass and shows no signs of vulcanization with respect to its physico-mechanical properties. Conversely, cases are known where the chemical combination of sulfur proceeds only feebly (and which with chloroprene rubber is entirely unnecessary), whereas the physico-mechanical effects of vulcanization are well pronounced. We therefore undertook an investigation of the processes of chemical combination of sulfur and changes in the solubility of rubber on heating its mixtures with sulfur in atmospheres of various gases. For these vulcanization tests, a mixture of rubber with 7% sulfur and 0.4% magnesium carbonate in the form of sheets of 0.5 mm. thickness containing 6.5% sulfur was used. A piece of such a sheet was wound in one layer around the glass tube *A* and was then inserted into the test tube *B*. Gas was slowly conducted at the top of the tube *A* escaping through the side tube of the test tube *B*. In the vulcanization tests in alcohol, water and formaldehyde solution, the liquid was poured into the test tube *B*, and on evaporation filled the entire space of the tube. All gases were previously dried. Where the presence of water is indicated in Table I, the gas without drying was bubbled through water contained in a Tishchenko flask before passing into the test tube. After expulsion of the air, the test tube was fitted into a long-neck, round-bottom flask containing at the bottom boiling xylene (b. 135-8°). The xylene vapors rising above the level of the rubber sheet maintained vulcanization at a constant temperature. The duration of vulcanization was counted from the time of immersion of the tube into the xylene vapors. A piece of the vulcanized rubber was worked up on rolls and analyzed to determine the free sulfur. From

TABLE I
THE GASES ARE ARRANGED ACCORDING TO INCREASING VALUES OF THE VULCANIZATION
CONST. K

Expt. No.	Gas	Time of Heating in Hrs.	Per Cent Free S	$K = \frac{1}{t} \log$	Total S Free S _i Mean
1	SO ₂	1	5.63	0.00103	0.00099
		2	5.06	0.00095	
2	H ₂ O vapor	1	5.53	0.00117	0.00103
		1.5	5.33	0.00090	
3	H ₂	2	4.92	0.00100	0.00117
		1	5.47	0.00124	
4	Air	1.5	5.06	0.00121	0.00118
		2	4.90	0.00106	
5	Ethyl alc.	1	5.44	0.00122	0.00120
		1.5	5.07	0.00126	
6	N ₂	2	4.86	0.00105	0.00124
		1	5.45	0.00127	
7	CO ₂	2	4.75	0.00113	0.00134
		1	5.43	0.00130	
8	CO ₂ + H ₂ O	2	4.69	0.00118	0.00138
		1	5.34	0.00142	
9	CH ₂ O + H ₂ O	1.5	5.03	0.00124	0.00146
		2	4.53	0.01136	
10	H ₂ + H ₂ O	1	5.24	0.00156	0.00154
		2	4.47	0.00121	
11	Vacuum	1	5.31	0.00145	0.00170
		2	4.34	0.00146	
12	NH ₃	1	5.19	0.00163	0.00239
		2	4.34	0.00146	
13	NH ₃ + H ₂ O	1	5.20	0.00173	0.00278
		2	4.09	0.00168	
14	H ₂ S	1	4.58	0.00255	0.00294
		1.5	4.00	0.00233	
15	H ₂ S + H ₂ O	2	3.50	0.00230	0.00361
		1	4.54	0.00259	
		2	2.86	0.00297	
		1	4.32	0.00297	
		1.5	3.45	0.00300	
		2	2.96	0.00285	
		1	4.05	0.00342	
		2	2.27	0.00380	

a mean value of two determinations the velocity constant of the vulcanization was calculated by the formula:

$$K = \frac{1}{t} \log \frac{\text{total } S}{\text{free } S_i},$$

assuming the total sulfur at 6.5%. To obtain an idea of the physical characteristics of the vulcanizates, their swelling in commercial amyl acetate was investigated. The vulcanized samples were extracted with acetone, then dried, weighed, macerated in amyl acetate for a definite time, removed, dried with filter paper, weighed and macerated again in the same solvent for further swelling. The calculations of the percentage increase in weight are based on the weight of samples used.

TABLE II

The Gases, in Which the Samples Were Heated, Are Arranged in the Order of the Increasing Percentage of Swelling, *i. e.*, in the First Place Are Given the Gases Which on Vulcanization Show the Greatest Influence on the Reduction of Rubber Solubility

Swelling Time 2 Hrs.				Swelling Time 4 Hrs.			
Vulcanizing Time 1 Hr.		Vulcanizing Time 2 Hrs.		Vulcanizing Time 1 Hr.		Vulcanizing Time 2 Hrs.	
Gas	Per Cent Swelling	Gas	Per Cent Swelling	Gas	Per Cent Swelling	Gas	Per Cent Swelling
H ₂ S	109	H ₂ S	94	H ₂ S	115	H ₂ S	103
CH ₂ O	114	NH ₃	97	NH ₃	134	SO ₂	112
NH ₃	124	SO ₂	93.4	CH ₂ O	134	NH ₃	114
H ₂	124	H ₂	122	CO ₂	152	H ₂	136
SO ₂	131	CH ₂ O	123	H ₂	152	Alc.	139
CO ₂	137	Air	131	SO ₂	155	CO ₂	142
H ₂ O	144	Alc.	131	Air	178	CH ₂ O	144
Air	152	CO ₂	135	H ₂ O	174	Air	160
Alc.	169	H ₂ O	145	Alc.	179	H ₂ O	174

Swelling Time 6 Hrs.				Swelling Time 24 Hrs.			
Vulcanizing Time 1 Hr.		Vulcanizing Time 2 Hrs.		Vulcanizing Time 1 Hr.		Vulcanizing Time 2 Hrs.	
Gas	Per Cent Swelling	Gas	Per Cent Swelling	Gas	Per Cent Swelling	Gas	Per Cent Swelling
H ₂ S	116	H ₂ S	104	H ₂ S	119	H ₂ S	107
NH ₃	132	SO ₂	116	NH ₃	127	NH ₃	121
CH ₂ O	134	NH ₃	119	CH ₂ O	130	SO ₂	140
CO ₂	154	H ₂	139	CO ₂	161	Alc.	138
H ₂	156	Alc.	141	H ₂	165	CH ₂ O	140
SO ₂	159	CO ₂	142	SO ₂	165	H ₂	141
Air	179	CH ₂ O	144	Alc.	165	CO ₂	143
Alc.	181	Air	162	Air	166	Air	152
H ₂ O	188	H ₂ O	189	H ₂ O	195	H ₂ O	158

The tabulated results show that the atmospheres of hydrogen sulfide and ammonia are sharply distinguished by their favorable action on the combination of sulfur, as well as on the physical properties of the vulcanizate. Water and sulfur dioxide reduce the percentage of combined sulfur, but sulfur dioxide on prolonged heating has good influence on the physical properties of the rubber, as can be seen in Table II, where the sample vulcanized in an atmosphere of sulfur dioxide for 2 hours stands in the third and second place. The velocities of the combination of sulfur of samples heated in atmospheres of a series of substances, such as hydrogen, nitrogen, carbon dioxide, alcohol vapors and formaldehyde solution, differ but little from the velocity during vulcanization in air. However, the physical properties of the vulcanizate are adversely affected by the air. The same undesirable effect is produced to a greater degree by water vapors under all conditions and by alcohol vapors under some conditions.

Since vulcanization at reduced pressure resulted in a marked increase of combined sulfur, this method was investigated more thoroughly, *i. e.*, a series of vulcanization tests were carried out at various reduced pressures, and the vulcanizates obtained were analyzed for

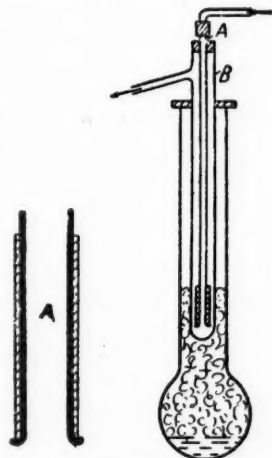


Figure 1

their percentage of combined sulfur and chloroform-extractable matter. In these tests light crepe sheet containing 5% sulfur was used. Vulcanization was carried out for 2 hours by the same technique as used in the preceeding experiments.

TABLE III

Residual Pressure in Mm.	Per Cent Free S	$K = \frac{1}{t} \log \frac{\text{total } S}{\text{free } S_t}$	Per Cent CH ₂ Cl Extract
760	4.10	0.00072	24.65
650	3.99	0.00082	19.21
500	3.77	0.00102	19.27
350	3.71	0.00107	20.27
200	3.82	0.00097	18.94
150	3.54	0.00124	14.90
100	3.33	0.00147	16.60
75	2.57	0.00238	14.12
60	12.34
50	7.97
25	2.22	0.00297	..
20	7.42

The results which are given in Table III show that an increased vacuum promotes vulcanization, *i. e.*, accelerates the rate of sulfur combination and decreases the solubility of the rubber. At the same time, the percentage of chloroform extract is greatly reduced and the constant of vulcanization is increased almost four-fold, *viz.*, from $K = 0.00072$ at 760 mm. pressure to $K = 0.00297$ at 25 mm. The vulcanization is particularly improved at pressures below 100 mm. The vulcanizate obtained in these tests was filled with minute bubbles, making it impossible to apply the swelling method for a study of the changes in the physical properties of rubber, as it was done in the preceeding series of experiments.

The results demonstrate conclusively the influence of the vulcanization medium on the two basic phenomena of the process, *viz.*, chemical combination of sulfur and physical changes in the rubber. Only atmospheres of hydrogen sulfide and ammonia had a favorable influence on these two processes in vulcanization. All other gases only either accelerate the combining of sulfur or reduce the solubility of rubber. Such a different action of separate gaseous media on the two chief processes of vulcanization may be caused by the action of the gases on the physical properties of sulfur and rubber. An investigation is being carried on to elucidate these questions. It is unnecessary to emphasize that this problem is of great importance in explaining the mechanism of acceleration of vulcanization by so-called accelerators.

The Coefficient of Friction of Rubber

J. B. Derieux

Coefficient of friction is defined as the ratio of the force of friction to the load producing it. The accepted laws of the coefficient of friction are:

1. It is independent of the area of the surface in contact.
2. It is independent of the load applied.
3. It is independent of the velocity, at low values.
4. The static value is greater than the kinetic, *i. e.*, it is greater at the beginning of motion than after motion has been established.

The accompanying data will show that every one of these accepted laws are violated by rubber.

The following values for area were obtained by varying the pressure in an automobile tire in place on an automobile on concrete.

Pressure in Pounds	Area in Sq. In.	Friction in Pounds	Load in Pounds	Coefficient
35	13	416	700	0.59
30	15	428	700	0.61
25	18	439	700	0.63
20	23	453	700	0.65
15	30	461	700	0.66
10	45	470	700	0.67

It will be observed that the coefficient increases with area.

The study of the effect of different loads was made by pulling a piece of automobile tire slowly along a level surface in the laboratory. The following values were obtained:

Load in Grams	On Varnished Wood		On Smooth Concrete		On Rough Concrete	
	Friction in Grams	Coefficient	Friction in Grams	Coefficient	Friction in Grams	Coefficient
700	300	0.428	605	0.865	615	0.878
900	400	0.445	785	0.873	805	0.895
1100	500	0.455	975	0.877	1000	0.910
1300	600	0.462	1175	0.905	1230	0.947
1500	700	0.467	1375	0.918	1550	1.064

It is evident that the coefficient increases with load increase.

The investigation of the effect of velocity was made by timing a piece of automobile tire in sliding with constant velocity down an inclined plane, and taking the tangent of the angle of the plane with the horizontal as the coefficient. (This is a standard method of finding the coefficient.)

It was found that rubber moves with a creeping motion down an inclined plane, and that gave the suggestion of the method of attack of the velocity problem. Setting the plane at an angle too small for the rubber to slide, apparently, it was observed to be very slowly creeping down the plane. The angle was increased, and while the rubber moved faster, it was without acceleration. The following data were obtained:

Smooth Surface					Rougher Surface				
Plane Length cm.	Angle deg.	Time	Vel. sec. cm./sec.	Coeff.	Plane Length cm.	Angle deg.	Time	Vel. sec. cm./sec.	Coeff.
25	18	Infin.	0	0.325	25	21	Infin.	0	0.384
25	20	74	0.338	0.364	25	22 $\frac{1}{2}$	122	0.205	0.414
25	22 $\frac{1}{2}$	20	1.25	0.414	25	25	21.6	1.16	0.466
25	25	6.4	3.90	0.466	25	27 $\frac{1}{2}$	8.0	3.12	0.520
25	27 $\frac{1}{2}$	2.7	9.25	0.520	25	30	2.45	10.2	0.578

It may be seen that the coefficient increases with velocity.

The relation of the static to the kinetic is obtained from the last preceding table. The static value is that for zero velocity, while the kinetic includes all the others. It is clearly seen that the static value is smallest.

The Specific Gravity of Rubber in Latex

O. de Vries

GRONINGEN, HOLLAND

In a study on the specific gravity of preserved latex, Rhodes¹ comes to the conclusion that the specific gravity of rubber in latex may be estimated at 0.902, and that the figure of 0.914, found by us several years ago,² and the figure of 0.912 used as a basis for the tables in the contracts of the Rubber Trade Association of London, are high. Rhodes's figure is based on a large experimental material (852 samples of preserved latex from nine different estates), and agrees well with the estimated figure of 0.901, to which Scholtz and Klotz³ came from 85 observations on fresh latex in Malaya.

Our figure was based on a large number of observations on normal estate latex, as well as on latex from specially tapped groups of trees; the difference between 0.902 and 0.914 is too large to be ascribed to experimental errors, though these of necessity are rather high, as the specific gravity of rubber can only be calculated by extrapolation over a zone much greater than the experimental zone itself. It seems of sufficient interest to subject these deviating results to a closer study, as this may, perhaps, throw some further light on a rather complicated problem which is not without practical interest.

Starting our investigations in the years 1916-1919, we had to reckon with different factors that might complicate the problem. It was not to be expected that the serum of different trees or plots of trees would show the same composition; physiological factors were sure to influence its content of proteins, mineral substances, and so on. Whether the specific gravity of rubber in latex was subject to variations, according to age of trees, size of rubber globules, content of proteins, etc., was far from clear at the outset. Moreover, complications were caused by the admixture of water, accidentally by rain, wet cups, or buckets, or intentionally by the tappers, in that period when there were managers prepared to swear that their trees yielded a latex of 10-15% original rubber content, so common was dilution from one cause or another. We, therefore, began our observations without any preconceived supposition, collecting a large number of observations. It was easy to state that mixtures of latex and water follow the "mixing rule" (straight ratio between specific gravity and content). The study of the relations between specific gravity and rubber content in pure latex gave somewhat more trouble, because pure serum and pure rubber could not be investigated. In that time latex was still regarded as a liquid from which the rubber could not be separated by centrifuging; but even at present, now that centrifuging has become a common process, it is still impossible to separate the two phases in a pure form suitable for exact determinations of physical properties. Some agent has to be used, and as a result we get neither the pure serum nor the pure rubber. It should not be forgotten that what we call "specific gravity of the rubber in latex" is in reality an imaginary figure, giving the specific gravity of a mixture not existent as such in the latex, but formed during coagulation and consisting of rubber globules, acid coagulable proteins, and substances absorbed by them according to the composition of the liquid phase (serum), the subsequent washing process, and so

on. Scholtz, therefore, uses the, at first somewhat striking, term of "crepe content of latex," and one might, in accordance with this line of thought, perhaps better speak of the specific gravity of crepe rubber in latex, meaning that the figure is calculated for rubber of crepe composition.

In our investigations we mixed known volumes of latex (200 cc.) and of 2½% acetic acid (40 cc.), the specific gravities of which were first determined; the specific gravity of the clear serum was then determined, and this was recalculated to original serum.⁴ From the specific gravity of the serum, determined in this way, and the specific gravity of the latex, the specific gravity of the rubber could be calculated. From numerous determinations on plots in different conditions

(age, tapping system, and so on) it was found that the specific gravity of the serum and the rubber both vary slightly according to circumstances; a graph was drawn up representing the relationships for pure latex of different rubber content and the mixtures obtained by diluting with water.⁵

In presenting this picture schematically and in its simplest form in our book, "Estate Rubber" (page 40), we made a slip and wrote about "rubber content in percentage of weight" (i. e., grams of rubber per 100 grams of latex). This slip was soon discovered during further investigations, and put right in a following publication (*Arch. Rubbercultuur*, 10, 19 (1926)): the points for specific gravity of a mixture, the content of which is given in percentage of volume

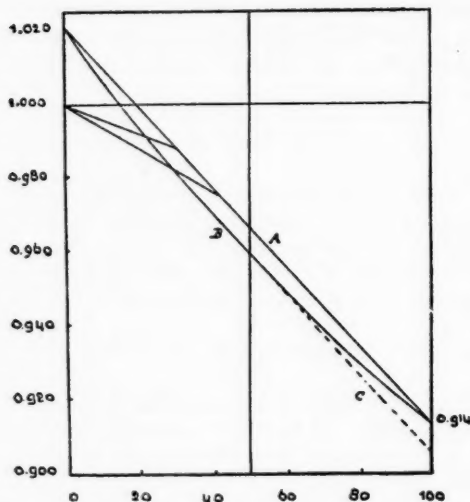


Figure 1—Specific Gravity of Latex Plotted against Rubber Content

Straight line A for rubber in percentage of volume; slightly curved line B for rubber in percentage of weight of latex; dotted line C probable extrapolation.

(i. e., cc. rubber on 100 cc. of latex), lie in a straight line (A in Fig. 1), as may be easily deduced from the formula: weight = volume \times specific gravity. When the content is calculated as percentage of weight, the points for specific gravity do not form a straight line, but a slightly curved line (B in Fig. 1).

The same oversight has been made, both by Scholtz and Klotz, and by Rhodes; in their investigations the rubber content of the latex was determined as percentage of weight, and the line for specific gravity and content is erroneously extrapolated as a straight line. The formula connecting specific gravity (S) of latex (l), rubber (r), and serum (s), with percentage of weight (c) is as follows:

$$S_1 = \frac{(c_r + c_s)s_r s_s}{c_r s_s + c_s s_r}$$

In our own experimental material, when using percentages of weight, extrapolation (dotted line C in Fig. 1) would have given a figure for specific gravity of rubber of 0.908 instead of 0.914, therefore 0.006 lower. As it interested us to know the result in Rhodes's case, we calculated his figures by means of the above

formula. Any two observations (Rhodes's Table I or V) may be used to calculate the specific gravity of rubber and that of serum; to make matters easier, we made the calculations for only two pairs, namely, his figure for average estate latex with 40% rubber (being probably one of the most normal and reliable), and for latices with 33 $\frac{1}{3}$ % and 50% rubber, respectively. This gave us the following approximate figures:

From 40% and 33 $\frac{1}{3}$ %	$S_{\text{rubber}} = 0.9072$	$S_{\text{serum}} = 1.0195$
From 40% and 50%	$S_{\text{rubber}} = 0.9057$	$S_{\text{serum}} = 1.0207$
Average	0.9065	1.020

Accurate figures might be obtained by using all of Rhodes's eleven points; but the above approximation is sufficient to conclude that Rhodes's figure for the specific gravity of rubber in latex should be corrected to about 0.9065 (or about 0.0045 unit higher, in good agreement with our former result of 0.006).

This brings the two figures, 0.914 and 0.9065, closer together, but it still leaves a rather large margin. It seems probable that this, at least partly, may be explained in the following way.

The rubber tree yields a latex of different composition, according to the physiological conditions it has to meet, consisting principally of its own condition (age, health, etc.), and the treatment it is subjected to. We found⁶ the general rule to be: the more drastic the treatment, the lower the rubber content of the latex, the lower the total solids in serum (the specific gravity of serum), the higher the nitrogen and ash content of the crepe, the larger the rate of cure, and the lower the viscosity of the crepe. Longer tapping cuts, more tapping cuts, shorter tapping intervals, deeper tapping, pollarding the trees, tapping younger trees as compared with older ones, all have a tendency in the above direction.

In these and other investigations we used latex from plots of trees tapped according to different systems; from mild to drastic, as understood in those days, the figures⁷ that interest us here are:

TABLE I

	Rubber Content of Latex	Specific Gravity of Rubber	Specific Gravity of Serum
1 cut daily over $\frac{1}{8}$ circumference	33.65	0.9135	1.0226
2 cuts daily over $\frac{1}{4}$ circumference	31.2	0.913	1.0223
2 cuts daily over $\frac{1}{4}$ circumference	29.15	0.914	1.0219
2 cuts daily over $\frac{1}{2}$ circumference	26.6	0.916	1.0207
2 cuts daily over $\frac{3}{4}$ circumference	22.6	0.918	1.0188
2 cuts daily over $\frac{1}{1}$ circumference	22.25	0.918	1.01895

Allowing for errors and uncertainties, there is a tendency for the calculated specific gravity of the rubber to decrease slightly, as the treatment is less severe and the rubber content of the latex higher. This seems quite comprehensible, for in coagulation a certain amount of protein from the serum is precipitated with the rubber, and as the protein content of the serum does not change very much because of more drastic or more mild treatment, the amount precipitated with the rubber and included in the crepe must be proportionately higher when the ratio serum-rubber is higher. These proteins have a higher specific gravity than the rubber hydrocarbon (they sink in the serum, while the rubber globules float in it), so that the calculated specific gravity of "crepe in latex" will be higher for heavily tapped trees. This is probably not the only cause, as may be easily seen when taking the difference in specific gravity between protein and hydrocarbon at about 0.2 and the increase in protein content at, say 1%; but the amount of minerals and other substances also increases.

Since the time of our investigations tapping systems have changed considerably, and alternate day or periodical tapping have come into vogue; the rubber content of original latex, which in the years of daily tapping was 28-33%, and seldom reached 35%, is now given, both by Scholtz and by Rhodes, as 37-43% normally, rising in not infrequent cases (for instance, in 15% out of Rhodes's observations) to 46-50%. When we plot our figures (see Fig. 2) and, uncertain as they may be, extrapolate to higher rubber contents, a figure of 0.907-0.909 for 40% latex does not at all seem improbable. It would be very interesting if the specific gravity of rubber from trees under different physiological conditions, yielding latex of high as well as of low rubber content (for instance, daily yields from a plot in periodic tapping) could be determined, so that the above mentioned conclusions

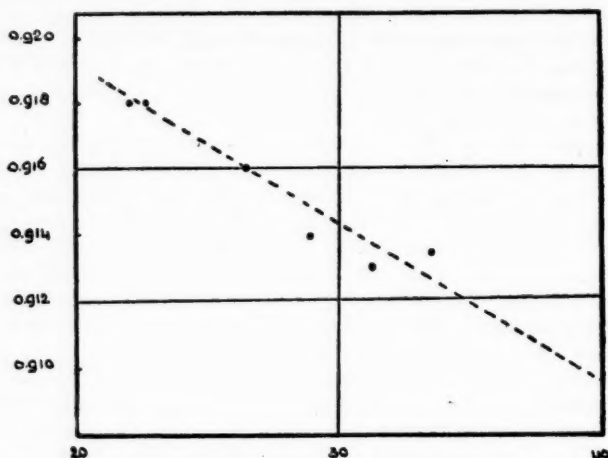


Figure 2—Specific Gravity of Rubber in Latex of Different Original Rubber Content. Dots: Figures from Table I

as to the physiological condition of the tree and its influence on the properties and composition of latex and rubber could be verified for present day conditions.

Attention may be drawn to the figure of 1.020 which we estimated from Rhodes's observations for the specific gravity of serum. Addition of ammonia solution and dilution of the latex with small amounts of water, which Rhodes mentions as probable, both would tend to lower the specific gravity of the serum, so that the original, undiluted latex would have shown a figure higher than 1.020. In our investigations we found figures between 1.016-1.025, and estimated 1.020 as a normal value; trees under a mild tapping system and showing a high rubber content of the latex may be expected to give a serum with rather high specific gravity (see Table I), so that a figure, higher than that calculated by Rhodes, seems to agree very well with what one would have expected.

There may be several other factors responsible for small changes in specific gravity of the rubber phase, causing small differences between Rhodes's figures and ours. For instance: the addition of ammonia may perhaps have an effect on the composition and the specific gravity of the rubber (what is its effect on the weight of crepe obtained from the latex?). An investigation would have to be made as to the effect on the specific gravity of the rubber of letting the precipitate of ammonium magnesium-phosphate and other substances (the sludge) settle out. And further,

the difference would have to be taken into account between fresh ammoniated latex in the East, as investigated by Rhodes, and latex in Europe, as it probably should form the basis for the tables of the Rubber Trade Association of London, and in which the crepe content, according to Bishop and Fullerton,³ is about 1% lower.

It seems an interesting task for the competent investigators in the East and in Europe to follow up these issues, which may contribute much to elucidate different points, and bring us a better knowledge of the properties of latex rubber, which in recent years has made such a remarkable progress as a commercial form of rubber.

References

- ¹ *J. Rubber Research Inst. Malaya*, **5**, 234 (1934).
- ² *Estate Rubber*, p. 38 (1920); *Arch. Rubbercultuur*, **3**, 183, 202 (1919).
- ³ *Kautschuk*, **7**, 144 (1931).
- ⁴ See *Arch. Rubbercultuur*, **1** (1917), English text page 277 and figures in Tables XIV-XXVIII; formula in *Arch. Rubbercultuur*, **3**, 189, 204 (1919).
- ⁵ *Estate Rubber*, **1920**, 40, 112.
- ⁶ *Ibid.*, Chap. II and page 589.
- ⁷ See *Arch. Rubbercultuur*, **3**, 199 (1919).
- ⁸ *Planting Manual*, No. 4 (1932), page D 10.

The Specific Gravity of Preserved Latex

Edgar Rhodes

The *Journal of the Rubber Research Institute of Malaya*, 5, 234 (1934), contained a paper¹ on the specific gravity of preserved latex written by the writer of this note. The paper has recently been made the subject of constructive comment by de Vries.²

As a result of the examination of 852 samples of preserved latex, a specific gravity/dry rubber content table was derived for preserved natural latices, and the dry rubber content range covered was wide enough to include natural unconcentrated latex in all the phases in which it is likely to be required by or become available to the commercial user. By the unavoidable expedient of extrapolation from the experimental results, a value of 0.902 was also derived for the specific gravity of the rubber phase in preserved latex. This value was in good agreement with the figure of 0.901 obtained by Scholtz and Klotz³ for "rubber" in fresh latex. On the other hand, de Vries,^{4,5} working with fresh latex had previously derived a value of 0.914 for the specific gravity of the rubber phase, and the specific gravity table used by the Rubber Trade Association of London for preserved latex gives on straight line extrapolation a value of 0.912. It seemed that the value indicated by the work of De Vries and that deduced from the table of the Rubber Trade Association were probably rather high, and certain experiments with centrifugal concentrated and centrifugal concentrate-skim mixtures were cited which provided some confirmatory evidence of this conclusion.

In his recent communication to the *India-Rubber Journal*,* de Vries has pointed out that Rhodes, like Scholtz, determined dry rubber contents as weight percentages, and extrapolated the relationship between these values and specific gravity as a straight line; he makes the point that this procedure is not strictly accurate, for whereas the relationship between the dry rubber content of a latex when expressed as a volume percentage, and its specific gravity can be represented by a straight line, the relationship between specific gravity and dry rubber content expressed as a weight percentage is not a linear one, and takes the form of a very slightly curved line. The effect of the slight curvature would be to give a higher result for the specific gravity of the rubber phase. He suggests, therefore, that the value of 0.902 derived by Rhodes as a result of straight-line extrapolation is probably slightly low. The formula

$$S_l = \frac{(C_r + C_s) S_r S_s}{C_r S_s + C_s S_r}$$

- S_l = specific gravity of latex
- C_r = weight percentage rubber
- C_s = weight percentage serum
- S_r = specific gravity rubber phase
- S_s = specific gravity serum phase

covers the relationship between the specific gravities of the rubber and serum phases, the weight percentage of dry rubber and the specific gravity of the whole latex, and by applying it to two pairs of the experimental results published by the

* See preceding article.

writer, de Vries has estimated that a value of 0.9065 for the specific gravity of the rubber phase is probably more accurate than the published figure of 0.902.

The criticism made by de Vries is sound, and it is necessary to correct for the non-linear relationship between weight percentage of dry rubber and the specific gravity of the latex. The experimental results are accordingly analyzed in the following pages in the light of de Vries' suggestion.

The Specific Gravity of the Rubber and Serum Phases of Latex

The experimental group-mean points which appear in Table II of the original publication¹ are set out below for easy reference; from these it is possible to calculate values for the specific gravity of "rubber" and serum using the formula

$$S_t = \frac{(C_s + C_r)(S_r S_s)}{C_r S_s + C_s S_r}$$

to which reference has been made earlier.

TABLE I

Group D.R.C. Per Cent Dry Weight	Total Samples in Group	Mean D.R.C. Per Cent by Weight	Mean Specific Gravity
28.1-30.0	97	29.3	0.9831
30.1-32.0	116	31.0	0.9820
32.1-34.0	47	33.0	0.9796
34.1-36.0	59	35.2	0.9773
36.1-38.0	117	37.3	0.9744
38.1-40.0	102	39.1	0.9725
40.1-42.0	104	40.9	0.9706
42.1-44.0	39	43.0	0.9682
44.1-46.0	38	45.2	0.9650
46.1-48.0	85	47.1	0.9626
48.1-50.0	48	48.8	0.9614

A value for the specific gravity of the rubber phase and a value for that of the serum phase can be obtained by calculation from any pair of the results in Table I. There are eleven group-mean points, so that it is possible to choose fifty-five different combinations of two D.R.C. points for purposes of calculation. In making his rough estimate of the probable specific gravity values, de Vries made calculations from two pairs only. In order to arrive at an accurate value it is necessary, as he suggests, to take the average of a larger number of pairs. Calculations have been made from fifty-three of the fifty-five possible pairs, and an average value for the specific gravity of the rubber phase and that of the serum phase obtained. The two pairs which were left out of consideration were the D.R.C. pairs 29.3-31.0 and 47.1-48.8, which lie at the extreme ends of the D.R.C. range. Every other possible combination was included in the calculation. Table II gives a list of the combinations and the values obtained.

It will be seen that the final average value for the specific gravity of the rubber phase is 0.9064, and that for the serum phase 1.0200. The value of 0.9019 for the specific gravity of the rubber phase is, therefore, corrected to 0.9064.

It now becomes necessary to discover whether or not this correction will have an appreciable effect on the table of figures published as Table V in the original publication¹ for normal preserved latex in the dry rubber content range 28-52%.

Specific Gravity Table for Normal Preserved Latex

By substituting the values 0.9064 and 1.0200 for S_r and S_s , respectively, in the formula to which reference has been made, it is possible to calculate values for the specific gravities of latices of any dry rubber content. In this way a specific

TABLE II

Calculation of values for specific gravity of rubber (S_r) and specific gravity of serum (S_s) from the eleven experimental points of Table I by the application of the formula:

$$S_i = \frac{(C_r + C_s) S_r S_s}{C_r S_s + C_s S_r}$$

Total Number of Pairs	D.R.C. Pairs		S.G. Rubber (S_r)	S.G. Serum (S_s)
	A	B		
1	29.3	33.0	0.9219	1.0108
2	29.3	35.2	0.9178	1.0129
3	29.3	37.3	0.9112	1.0164
4	29.3	39.1	0.9114	1.0160
5	29.3	40.9	0.9115	1.0161
6	29.3	43.0	0.9107	1.0165
7	29.3	45.2	0.9074	1.0183
8	29.3	47.1	0.9064	1.0187
9	29.3	48.8	0.9087	1.0176
10	31.0	33.0	0.9054	1.0206
11	31.0	35.2	0.9101	1.0181
12	31.0	37.3	0.9047	1.0212
13	31.0	39.1	0.9065	1.0200
14	31.0	40.9	0.9077	1.0194
15	31.0	43.0	0.9076	1.0196
16	31.0	45.2	0.9045	1.0212
17	31.0	47.1	0.9039	1.0217
18	31.0	48.8	0.9067	1.0201
19	33.0	35.2	0.9142	1.0156
20	33.0	37.3	0.9044	1.0212
21	33.0	39.1	0.9069	1.0199
22	33.0	40.9	0.9087	1.0197
23	33.0	43.0	0.9080	1.0192
24	33.0	45.2	0.9045	1.0215
25	33.0	47.1	0.9038	1.0218
26	33.0	48.8	0.9068	1.0199
27	35.2	37.3	0.8951	1.0286
28	35.2	39.1	0.9032	1.0229
29	35.2	40.9	0.9061	1.0207
30	35.2	43.0	0.9065	1.0205
31	35.2	45.2	0.9027	1.0232
32	35.2	47.1	0.9023	1.0236
33	35.2	48.8	0.9059	1.0210
34	37.3	39.1	0.9124	1.0156
35	37.3	40.9	0.9076	1.0104
36	37.3	43.0	0.9103	1.0161
37	37.3	45.2	0.9047	1.0108
38	37.3	47.1	0.9036	1.0222
39	37.3	48.8	0.9075	1.0191
40	39.1	40.9	0.9120	1.0156
41	39.1	43.0	0.9094	1.0178
42	39.1	45.2	0.9024	1.0234
43	39.1	47.1	0.9018	1.0239
44	39.1	48.8	0.9067	1.0199
45	40.9	43.0	0.9073	1.0198
46	40.9	45.2	0.8989	1.0273
47	40.9	47.1	0.8994	1.0269
48	40.9	48.8	0.9058	1.0212
49	43.0	45.2	0.8916	1.0353
50	43.0	47.1	0.8957	1.0310
51	43.0	48.8	0.9052	1.0215
52	45.2	47.1	0.9003	1.0259
53	45.2	48.8	0.9130	1.0127
53	Total		48.0388	54.0609
	Average Values		0.9064	1.0200

gravity table can be constructed on the basis of the corrected values for comparison with Table V¹ obtained originally from the straight line $S = -0.001158t + 1.0177$. In Table III this comparison is made.

TABLE III

Showing comparison of values for specific gravity derived from:

(a) The straight line $S = -0.001158t + 1.0177$ (Table V¹) and

(b) From the formula $S_t = \frac{(C_s + C_r) \times 0.9064 \times 1.0200}{C_r \times 1.0200 + C_s \times 0.9064}$

	D.R.C. Per Cent by Weight 1	Specific Gravity, from (a) above 2	from (b) above 3
	28.0	0.9853	0.9854
	29.0	0.9841	0.9842
	30.0	0.9830	0.9830
	31.0	0.9818	0.9819
	32.0	0.9806	0.9807
	33.0	0.9795	0.9795
	34.0	0.9783	0.9783
	35.0	0.9772	0.9771
	36.0	0.9760	0.9760
	37.0	0.9749	0.9748
Experimental zone—	38.0	0.9737	0.9736
	39.0	0.9725	0.9725
	40.0	0.9714	0.9714
	41.0	0.9702	0.9701
	42.0	0.9691	0.9690
	43.0	0.9679	0.9678
	44.0	0.9667	0.9667
	45.0	0.9656	0.9655
	46.0	0.9644	0.9644
	47.0	0.9633	0.9633
Extrapolation zone—	48.0	0.9621	0.9621
	49.0	0.9610	0.9610
	50.0	0.9598	0.9598
	51.0	0.9586	0.9587
	52.0	0.9575	0.9576
	53.0	0.9563	0.9564
	54.0	0.9552	0.9553
	55.0	0.9540	0.9542
	56.0	0.9529	0.9531
	57.0	0.9517	0.9520
	58.0	0.9505	0.9508
	59.0	0.9494	0.9498
	60.0	0.9482	0.9487
	61.0	0.9471	0.9476

The figures in lighter type are obtained by extrapolation beyond the experimental zone.

The values already published in Table V of the original publication¹ are set out in Column 2, while Column 3 gives the values derived from the corrected specific gravities of "rubber" and serum.

It is at once apparent that over the whole of the experimental zone, the two tables are to all intents and purposes identical, and that not until by extrapolation a dry rubber content of 57% is reached do appreciable differences begin to be apparent.

In Table IV of the original publication,¹ figures were given for the closeness of approach of the experimental points to the line $S = -0.001158t + 1.0177$, and

these are again set out in Table IV below in comparison with values derived from the corrected specific gravities for "rubber" and serum.

TABLE IV

Closeness of approach of the group-mean points to:

- (a) The line $S = -0.001158t + 1.0177$ (Table IV¹) and
(b) Values derived from the formula:

$$S_t = \frac{(C_s + C_r) \times 0.9064 \times 1.0200}{C_r \times 1.0200 + C_s \times 0.9064}$$

Mean D.R.C.	Mean S.G. Experi- mental	S.G. Calc. from (a) above	Deviation from Exptl. S.G.	S.G. Calc. from (b) above	Deviation from Exptl. S.G.
29.3	0.9831	0.9818	+0.0007	0.9839	+0.0008
31.0	0.9820	0.9818	-0.0002	0.9819	-0.0001
33.0	0.9796	0.9795	-0.0001	0.9795	-0.0001
35.2	0.9773	0.9769	-0.0004	0.9769	-0.0004
37.3	0.9744	0.9745	+0.0001	0.9744	Nil
39.1	0.9725	0.9724	-0.0001	0.9724	-0.0001
40.9	0.9706	0.9703	-0.0003	0.9703	-0.0003
43.0	0.9682	0.9679	-0.0003	0.9678	-0.0004
45.2	0.9650	0.9654	+0.0004	0.9653	+0.0003
47.1	0.9626	0.9632	+0.0006	0.9632	+0.0006
48.8	0.9614	0.9612	-0.0002	0.9612	-0.0002

It will be seen that there is no appreciable difference between the closeness of approach of the two sets of calculated values to the experimental points. It is, therefore, clear that the original specific gravity table is accurate in the D.R.C. range 28-52%, which covers all commercial requirements for unconcentrated preserved latex. The straight line $S = -0.001158t + 1.0177$ does, in fact, give an accurate picture of the results over the whole experimental range.

It is next required to consider whether or not the substitution of the corrected value for the specific gravity of the rubber phase of latex, weakens materially the deductions which were made in the original publication from the experimental work on settled latex and centrifugal concentrates.

The Specific Gravity of Settled Latex, Centrifugal Concentrates, and Centrifugal Concentrate-Skim Mixtures

(a) *Settled Latex and Individual Samples of Concentrate*.—In Section B of the original publication¹ it was shown that by simple gravitational settlement of

TABLE V

Deviation of the specific gravities of centrifugal concentrates from:

- (a) The line $S = -0.001158t + 1.0177$ (Table VII¹) and
(b) Values derived from the formula:

$$S_t = \frac{(C_s + C_r) \times 0.9064 \times 1.0200}{C_r \times 1.0200 + C_s \times 0.9064}$$

Group D.R.C.	No. of Samples Examined	Mean D.R.C.	Mean S.G. Found	Calc. from (a)	Calc. from (b)	Deviation from (a)	Deviation from (b)
56.1-58.0	6	57.2	0.9476	0.9515	0.9518	-0.0039	-0.0042
58.1-59.0	10	58.6	0.9458	0.9498	0.9502	-0.0040	-0.0044
59.1-60.0	21	59.6	0.9442	0.9487	0.9491	-0.0045	-0.0049
60.1-61.0	31	60.4	0.9426	0.9478	0.9482	-0.0052	-0.0056
Average						-0.0044	-0.0048

sludge specific gravity differences of the order of -0.004 could be observed, and a series of sixty-eight samples of centrifugal concentrate were examined for dry rubber content and specific gravity in order to discover the deviation of the specific

gravity from that indicated for normal preserved latex by extrapolation of the straight line $S = -0.001158t + 1.0177$. It was found (see Table VII¹) that the deviation of specific gravity was of the same order, but in general slightly greater than that observed when normal preserved latex is allowed to undergo gravitational settlement. Table V reproduces Table VII of the original publication,¹ together with figures showing the deviation of the experimental results from the specific gravities which are calculated from the corrected values for "rubber" and serum.

The use of the corrected values for the specific gravity of "rubber" and serum, increases the deviations slightly, but they remain of the same order as those observed for the gravitational settlement of normal latex, namely, -0.004 to -0.005 .

It was further agreed that if the experimental specific gravity values for centrifugal concentrate had been related not to the values derived from the work under reference, but to those obtained by the extrapolation of the table of the Rubber Trade Association or to those of de Vries, the deviations observed would have been of the higher order of -0.01 . This argument is seen from Table V to require no modification.

With reference to the value of 0.912 derived from the R.T.A. table for the specific gravity of the rubber phase, it should be noted incidentally that this value is obtained by straight-line extrapolation, and since it is equally the practice of the Rubber Trade Association and the Rubber Research Institute to express dry rubber content as a weight percentage, the figure of 0.912 becomes subject to correction in order to make it comparable to the corrected value of 0.9064 now derived from the figures in Table I. When this correction is applied the approximate R.T.A. values for the specific gravities of the "rubber" and serum phases of latex become 0.916 and 1.0133, respectively.

(b) *Centrifugal Concentrate-Skim Mixtures.*—In the original publication, a series of mixtures were made from a quantity of a single centrifugal concentrate of 56.7% dry rubber and its own skim latex, of which the dry rubber content was 15.7%. Dry rubber content-specific gravity relations were obtained for the two primary materials and twelve different mixtures. From these figures a straight line extrapolation gave a value for the specific gravity of the rubber phase in this concentrate of 0.8966, which deviated by -0.0053 from the value of 0.9019, which had been similarly derived for "rubber" in normal preserved latex. This deviation was of the same order as that observed for settled lattices and individual samples of centrifugal concentrate. The substitution of the de Vries value of 0.914 on the R.T.A. value of 0.912 for the figure of 0.9019 would have given deviations of the order of 0.017 and 0.015, respectively, and this was taken as a further indication that the de Vries value and R.T.A. derived value were probably high.

The value of 0.8966 was derived by straight-line extrapolation from D.R.C. values expressed as a weight percentage, and it therefore requires to be corrected. The fourteen experimental points permit calculations of the specific gravity of the rubber disperse phase to be made from ninety-one different combinations of two D.R.C. points using the formula

$$S_i = \frac{(C_r + C_s) S_r S_s}{C_r S_s + C_s S_r}$$

and the average value for the specific gravity of the rubber phase in the latex concentrate is found in this way to be 0.9011, which deviates from the similarly corrected value of 0.9064 for rubber in normal preserved latex by -0.0053 . This deviation is identical with the figure obtained in the original publication.¹ The

deviations from the de Vries value of 0.914 and the corrected R.T.A. value of 0.916 are 0.13 and 0.15, respectively, which are also of the same order as those cited originally. The results obtained by the substitution of corrected for the original values do not, therefore, demand a change in the deductions which were originally made.

Discussion and Conclusions

At the instigation of de Vries, the experimental results which led to the deduction that the specific gravity of the rubber phase of preserved latex was 0.902 have been carefully re-examined, and the value is now corrected to 0.9064. The difference between this corrected value and de Vries' own figure of 0.914, obtained, it should be noted, on fresh latex, is still a large one, and of the order of 0.008. Similarly, the difference between the value of 0.9064 and the corrected value of 0.916 derived from the R.T.A. table remains of the order of 0.01. A re-examination of the supporting evidence advanced in Section B of the writer's original publication does nothing to weaken it, and the reasons for the differing results must for the present remain a matter for some conjecture. De Vries worked with fresh latex of low, dry rubber content at a time when it was by no means easy to obtain a rubber-rich material, and he has advanced this and a number of other factors which are possibly contributory to the difference between his final results and those now indicated. There can be no doubt that the specific gravity of the serum must be reduced by the addition of ammonia solution as a preservative. In the original publication no stress was laid on the value for the specific gravity of the serum, because it was felt that it could not be comparable with that of the fresh latex used by de Vries. In our work, however, no added water, except that which is contained in the ammonia solution itself, was present in the samples. De Vries indicates that a low value for the specific gravity of the rubber phase might be expected when the ratio rubber/serum is high, and also inquires what effect on the specific gravity of the "rubber" would be produced by allowing the latex to deposit its phosphates and sludge. Centrifugal concentration provides an artificial combination of the two effects, namely, that of increasing the ratio rubber/serum, and removing extraneous solid matter. In our work on individual samples of centrifugal concentrate this treatment is seen to result in specific gravities lower than those derived for normal latex of the same D.R.C., and in the work on concentrate-skim mixtures the derived value of 0.9011 for the rubber phase itself is also below that of 0.9064 for normal preserved latex. These experiments provide a general indication of the combined effect of the two factors mentioned, but they do not fully disentangle the effects due to each. It should be mentioned that the determinations made in our work were not made on freshly ammoniated samples. In the original paper¹ it was not pointed out that the samples were examined after periods of time varying from a week to three weeks; the exigencies of other work made it quite impossible to work to a standard storage period. It may be taken, however, that although the samples were not stored for such a long period after preservation as would be the case with latex available for experiments in Europe, they were not examined until the rapid initial changes in D.R.C. noted by Bishop and Fullerton⁶ had taken place, and the latex had reached the state in which subsequent change in D.R.C. is slow. In this respect, therefore, our work was not comparable with that of de Vries, and this may account in great part for the difference between his value for the specific gravity of the rubber phase and our own. If one considers the specific gravity table of the R.T.A. in conjunction with the corresponding values in Table III, it will be seen that although the R.T.A.

table is based on different values for the specific gravities of the ultimate rubber and serum phases of latex, the figures for commercial latices in the zone covered by the R.T.A. table differ but slightly from those set out in Table III. The values of the R.T.A. were presumably intended only for approximate commercial purposes, and it is unlikely that the differences which do show themselves will disturb either dealers or industrial users.

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Heats of Reaction of the System Rubber-Sulfur

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PREVIOUS investigators have employed two methods for determining the heat effects when rubber is vulcanized. In one method the heats of vulcanization are found by subtracting the heats of combustion of vulcanized rubber-sulfur compounds from the heats of combustion of the corresponding mixtures of rubber and sulfur before vulcanization (1, 10, 11). This method is limited in precision by reason of the fact that the differences thus obtained are at most only a few per cent of the measured heats of combustion. The other method, which has been used previously, involves the determination of the temperature rise which occurs when mixtures of rubber and sulfur are vulcanized. This method has, for the most part, been used for relative measurements, but Blake (2) has recently employed it for quantitative determinations of the heats of reaction of rubber with proportions of sulfur up to about 8 per cent by weight. Recently Daynes (7) has employed a similar method for measurements over a wider range of composition.

This investigation was undertaken for the purpose of measuring the heats of reaction of rubber with different percentages of sulfur over the entire range of composition in which combination takes place. The study was exploratory in character, the aim being to make the measurements by direct means with emphasis on simplicity rather than refinement of calorimetric procedure.

Description of Calorimeter

The calorimeter in which the reaction of rubber and sulfur was conducted consisted essentially of an insulated copper cylinder which serves as a constant-temperature bath. This cylinder was $2\frac{1}{4}$ inches (5.72 cm.) in diameter and $9\frac{1}{2}$ inches (24.13 cm.) long, and in it four holes were bored, $\frac{1}{4}$, $\frac{5}{8}$, $\frac{1}{2}$, and 1 inch (0.64, 1.59, 1.59, and 2.54 cm.), respectively, in diameter, and 9 inches (22.86 cm.) in depth. As shown in Figure 1, the cylinder was mounted in a 1-liter Dewar flask which was surrounded by thermal insulation and placed in a double-walled container. This container was maintained at constant temperature—about 175° C.—by means of vapors of boiling cymene.

The temperature of the calorimeter was indicated by a mercury-in-glass thermometer which was placed in the smallest hole, K. The thermometer was graduated to 0.1° C. and could be read to 0.01° by means of a magnifying glass. For the purpose of intro-

ducing heat into the calorimeter, a coil of nichrome wire having a resistance of about 40 ohms was supported on a glass tube and mounted in hole *H*. Current was supplied through copper leads; the current was measured by means of an ammeter, and the potential by a voltmeter. The flow of current was controlled by a manually operated switch, and the time was observed by means of a watch. A perforated brass cylinder was mounted in hole *A* and served as a receptacle for the $\frac{1}{4}$ -inch (0.64-cm.) steel balls which were dropped into the calorimeter to effect cooling. This cylinder was attached to a glass tube of the same diameter so that it could easily be removed. In order to minimize the loss of heat through this large tube, a smaller tube, slightly larger in diameter than the steel balls, was mounted in it and sealed in position, and the annular space was filled with insulation. A glass tube, *S*, mounted in hole *E*, served as a receptacle for the sample under test. This tube was sealed at the bottom and was closed at the upper end by a loosely fitting glass stopper, not shown in Figure 1, which extended down nearly to the top of the copper cylinder.

To facilitate the interchange of heat between the different elements and the copper block, a high-melting ceresin wax was placed in all four holes. The rate of transfer of heat from one part of the calorimeter to another was such that, when the temperature was changed a few degrees by introducing heat electrically or by putting in a cold sample, temperature equilibrium within the copper cylinder was reestablished within 3 or 4 minutes.

The equilibrium temperature of the calorimeter was about 1° C. below the temperature of the outer container, which was kept constant by means of boiling cymene. This difference was due to the loss of heat through the insulation above the calorimeter and also through the tubes leading to the outside. This relatively small loss of heat was so nearly constant during any given experiment as to occasion no appreciable error.

Preparation of Samples

The materials used in the present investigation were commercial pale crepe rubber, purified rubber, and powdered rhombic sulfur. The purified rubber was prepared by digesting latex with steam at an elevated temperature and subsequently extracting products of hydrolysis of proteins and the resins with alcohol and water (19). The sulfur employed was a commercial grade of ground rhombic sulfur intended for use in rubber manufacture. Analysis indicated no impurities except a trace of ash. Mixtures of weighed quantities of rubber and sulfur were prepared in the usual way by means of either a roll mill or an internal mixer, care being exercised to avoid loss in the mixing process.

For the measurements of the heats of reaction, samples of rubber-sulfur mixtures were prepared in the form of cylinders about 10 mm. in diameter which could be slipped easily into the reaction tube of the calorimeter. The samples containing from 0 to 20 per cent of sulfur were formed in the desired shape by pressing the stock at about 100° C. in a rod mold lined with aluminum foil to prevent sticking. Samples of stocks containing more than 20 per cent of sulfur could not be used as solid cylinders of 10 mm. diameter, because local superheating along the axis of the cylinders occurred during

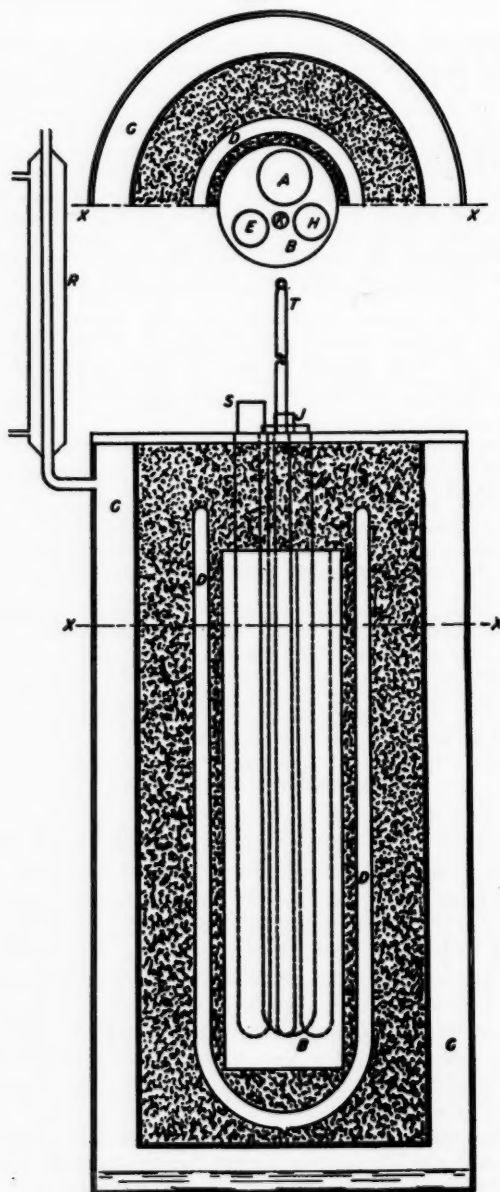


FIGURE 1. CROSS SECTION OF CALORIMETER FOR DETERMINATION OF HEATS OF REACTION

- A. Cavity for container of steel balls
- B. Copper cylinder
- C. Cymene vapor bath
- D. Dewar flask
- E. Cavity for sample tube
- H. Cavity for calorimeter heater
- J. Tube leading to container for steel balls
- K. Cavity for thermometer
- R. Reflux for cymene vapors
- S. Sample tube
- T. Mercury thermometer

the reaction between the rubber and the sulfur. These samples were made in the form of hollow cylinders by wrapping the rubber stock in sheet form around weighed glass tubes of about 4 mm. outside diameter. Correction for the heat capacity of these tubes was made in computing the results.

The samples which were vulcanized in the course of determining the heats of reaction were subsequently employed for the measurement of the differences in heat content of the rubber-sulfur compounds between room temperature and the temperature of the calorimeter.

Method of Determining Heats of Reaction

In order to determine the heats of reaction of rubber and sulfur at the vulcanizing temperature, about 175° C., by the method here employed, it was necessary not only to measure the heat effects at that temperature but also to measure the differences in heat content of the unvulcanized rubber-sulfur mixtures between the temperature of the room (approximately 25° C.) and that of the calorimeter. Furthermore, to obtain the heats of reaction at 25° C., it was necessary to measure also the differences in heat content of the vulcanized rubber-sulfur compounds between 175° and 25° C.

MEASUREMENT OF DIFFERENCES IN HEAT CONTENT BETWEEN 25° AND 175° C. The experimental procedure in the measurement of difference in heat content was the following:

Cymene was placed in the outer double-walled container of the apparatus and was heated to boiling by an electric hot plate. The copper cylinder was heated electrically to approximately the same temperature as the vapors of the boiling cymene and was allowed to stand for several hours until thermal equilibrium was established between the cylinder and the container. A sample of known weight and temperature, usually about 25° C., was slipped quickly into the sample tube of the calorimeter. The rubber samples were first dusted with talc to prevent their sticking to the sides of the glass tube. The weight of the talc used was not significant. Experiments in which the sample tube was opened and closed in the same manner without introducing a sample indicated that no significant quantity of heat was lost from the calorimeter in this operation. Heat was then added electrically to the copper cylinder in quantity sufficient to balance the heat taken up by the cold sample and bring it again to the previous equilibrium temperature. During this process the temperature variation was seldom greater than 1° C., and the time of disturbance never over 4 minutes, so the results were probably not materially affected by the onset of the vulcanization reaction.

The difference in heat content of a sample between the temperature of the room and that of the calorimeter was found from the equation:

$$(H_s - H_r) = \frac{EIs}{m}$$

where H_c, H_r = heat contents of samples at temp. of calorimeter and of room, respectively, joules/gram

s = time of heating, seconds

E = potential, volts

I = current, amperes

m = weight of sample, grams

Since the temperatures of the calorimeter and of the room are relatively close to 175° and 25° C., respectively, the difference in heat content between these temperatures, $(H_{175} - H_{25})$, can be computed from $(H_c - H_r)$ without appreciable error.

MEASUREMENT OF HEATS OF REACTION. In determining the heat of reaction of a mixture of rubber and sulfur, a cylindrical sample was dusted with talc and dropped into the sample tube of the calorimeter. The quantity of heat required to restore the calorimeter to the equilibrium temperature was computed and was added electrically. With this heat added, the calorimeter was ready for the measurement of the heat of reaction of the sample at the calorimeter temperature. Vulcanization proceeded with the liberation of heat. In order to determine this quantity of heat, steel balls at the temperature of the room were dropped into the calorimeter at such a rate as to keep the temperature constant. Since the balls were uniform in weight to within 0.1 per cent, it was necessary only to count them to obtain the mass of the metal added. The reaction, in all cases, was complete in about an hour, though observations of the temperature were made for at least one-half hour longer to insure that equilibrium had been reached.

The heat of reaction at the temperature of the calorimeter, in joules per gram of mixture, is given by the relation:

$$\Delta H_{175} = \frac{-1.045 N(0.510)(t_c - t_r)}{m}$$

where N = number of steel balls added

1.045 = weight in grams of each ball

m = weight of sample, grams

0.510 = mean heat capacity, in joules/gram/° C., of the steel from 25° to 175° C., which were approximately the temperatures of the room and of the calorimeter, t_r and t_c , respectively

The heat of reaction at 25° C. was calculated from the equation:

$$\Delta H_{25} = \Delta H_{175} + (H_{175} - H_{25})_{\text{unvulcanized}} - (H_{175} - H_{25})_{\text{vulcanized}}$$

where the last two terms represent differences in heat content between the temperatures indicated.

ILLUSTRATIVE EXPERIMENT. The data and results which were obtained in a typical experiment involving the measurement of heat of reaction and the differences in heat content between room temperature and vulcanizing temperature, of

the reactant mixture and the product of reaction, are given in Table I.

TABLE I. CALCULATION OF HEAT OF REACTION OF A RUBBER-SULFUR MIXTURE

State of Sample	Unvulcanized	Vulcanized
Compn. of sample:		
Rubber, per cent by weight	75.0	75.0
Sulfur, per cent by weight	25.0	25.0
Sulfur, atom/gram-mole C_5H_8 ^a	0.708	0.708
Weight of sample, grams	8.46	7.87
C_5H_8 in sample, gram-mole	0.0933	0.0868
Temp. of calorimeter, °C	176.2	178.2
Temp. of room, °C	24.0	24.3
Detn. of $(H_{175} - H_{25})$:		
Current, ampere	0.775	0.770
Potential, volts	30.8	30.9
Time, seconds	105	85
Heat added, joules	2,506	2,022
$(H_e - H_f)$, joules/gram of sample	296	257
$(H_{175} - H_{25})$, joules/gram of sample	292	250
$(H_{175} - H_{25})$, joules/gram-mole C_5H_8	26,500	22,700
Detn. of heat of reaction at 175° C.:		
Number steel balls added	38
Weight steel added, grams	39.7
Mean heat capacity of steel, joule/gram/°C	0.510
Total heat liberated by reaction, joules	3,081
$-\Delta H_{175}$, joules/gram of sample	364
$-\Delta H_{175}$, joules/gram-mole C_5H_8	33,000
Detn. of heat of reaction at 25° C.:		
$(H_{175} - H_{25})_{unvul.} - (H_{175} - H_{25})_{vul.}$, joules/gram-mole C_5H_8	3,800
$-\Delta H_{25}$, joules/gram-mole C_5H_8	29,200
$-\Delta H_{25}$, joules/gram sample	322

^a The computation of atoms of sulfur per gram-mole C_5H_8 was made as if the rubber were all C_5H_8 .

Results of Calorimetric Determinations

DIFFERENCES IN HEAT CONTENT BETWEEN 25° AND 175° C. The differences in heat content between 25° and 175° C. for the various samples are given in Table II. The average value of $(H_{175} - H_{25})$ for the rubber alone is 326 joules per gram, which is equivalent to a mean heat capacity of 2.17 joules per gram per °C. over this range. This value is of the same order of magnitude as other determinations reported in the literature (3, 8, 16, 21), the more reliable of which lie between 2.0 and 2.2 joules per gram per °C. Strict comparison cannot be made between these different values since they relate to different temperature ranges. The difference in heat content for sulfur between 25° and 175° C. was found to be 194 joules per gram.

Calculations from data given in the literature (18, 20) for the heat capacities of solid and liquid sulfur and the heat of fusion give a value of 191 joules per gram for this difference.

The differences in heat content between 25° and 175° C. of both unvulcanized rubber-sulfur mixtures and vulcanized rubber-sulfur compounds are shown in Figure 2 as functions

of the sulfur content in percentage by weight. For the unvulcanized mixtures a straight line was drawn between the values at 0 and 100 per cent of sulfur. This involves the assumption that the heat content of the mixture follows a simple additive relation and leaves out of consideration the heat of solution of rubber in sulfur and the interfacial energy between the rubber and the sulfur, both of which are probably very small.

Evidence of the linear relation between the differences in heat content of rubber-sulfur mixtures and the composition of such mixtures in percentage of sulfur by weight was obtained by observing the quantity of heat required to bring the calorimeter to the equilibrium temperature after a sample of mixture at room temperature had been added. This was not a precise determination because the liberation of heat by the vulcanization reaction became appreciable in a very few minutes, but, as shown in Figure 2, the observations are in fair agreement with the linear relation. The values for the rubber-sulfur compounds, also shown in Figure 2, cannot be adequately represented by a single linear equation. However, two linear equations intersecting at the composition 19 per cent of sulfur (0.5 atom of sulfur per gram-mole of C_5H_8)

TABLE II. DIFFERENCES IN HEAT CONTENT BETWEEN 25° AND 175° C. OF RUBBER, SULFUR, RUBBER-SULFUR MIXTURES, AND RUBBER-SULFUR COMPOUNDS

Composition of Sample			Difference in Heat Content, ($H_{175} - H_{25}$), joules/gram	
Rubber		Sulfur		
Condition	Per cent	Per cent	Atoms/gram- mole $C_5H_8^a$	
Purified	100	0	0	331
Purified	100	0	0	321
.....	0	100	...	191
.....	0	100	...	196
				Mix- ture
Purified	95.5	4.5	0.100	318
Crude	95.5	4.5	0.100	...
Purified	91.0	9.0	0.210	314
Crude	91.0	9.0	0.210	...
Purified	82.0	18.0	0.467	301
Crude	82.0	18.0	0.467	...
Crude	78.0	22.0	0.599	296
Crude	75.0	25.0	0.708	301
Crude	75.0	25.0	0.708	292
Crude	75.0	25.0	0.708	...
Crude	75.0	25.0	0.708	250
Crude	75.0	25.0	0.708	...
Crude	75.0	25.0	0.708	240
Purified	68.0	32.0	1.00	278
Crude	68.0	32.0	1.00	...
Crude	68.0	32.0	1.00	220
Crude	68.0	32.0	1.00	...
Crude	68.0	32.0	1.00	217
Crude	68.0	32.0	1.00	212

^a The computation of atoms of sulfur per gram-mole C_5H_8 was made as if the rubber were all C_5H_8 .

fit the results fairly well. This method of representation was chosen, since it is shown later in this paper that the heats of reaction indicate the formation of compounds above 19 per cent of sulfur dissimilar to those formed at lower percentages of sulfur.

It would be expected that a break in the heat content curve would most probably occur at this point, and the curve was drawn accordingly. The shape of the curve, however, does not materially affect the values obtained for the heat of vulcanization.

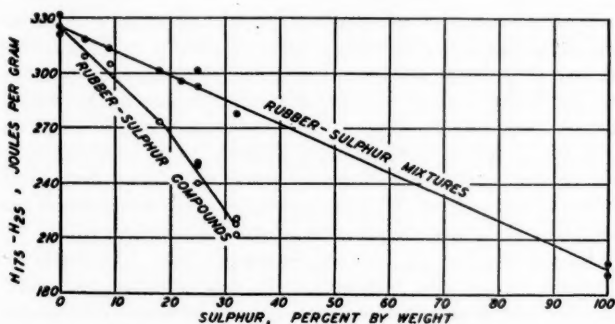


FIGURE 2. RELATION BETWEEN COMPOSITION AND DIFFERENCES IN HEAT CONTENT BETWEEN 25° AND 175° C. OF RUBBER-SULFUR COMPOUNDS AND MIXTURES

Equations were derived from the curves drawn in Figure 2 expressing the differences in heat content in kilojoules per gram-mole of C_5H_8 for compositions in terms of molecular ratios.¹ For the unvulcanized mixtures:

$$(H_{175} - H_{25}) = 22.2 + 6.2x \text{ kilojoules/gram-mole of } C_5H_8$$

where x = number of sulfur atoms/gram-mole C_5H_8 .

This equation holds true for all values of x . For the vulcanized rubber-sulfur compounds, from $x = 0$ to $x = 0.5$:

$$(H_{175} - H_{25}) = 22.2 + 1.2x \text{ kilojoules/gram-mole } C_5H_8$$

From $x = 0.5$ to $x = 1.0$:

$$(H_{175} - H_{25}) = 24.1 - 2.6x \text{ kilojoules/gram-mole } C_5H_8$$

The observations agree with the values indicated by these equations with a maximum deviation of 0.6 and an average deviation of 0.2 kilojoule per gram-mole of C_5H_8 .

The mean heat capacity between 25° and 175° C. was determined for the steel balls used to absorb heat from the calorimeter in the measurements of the heats of the reaction. The average value obtained was 0.510 joule per gram per °C. Levin and Schottky (17) give data from which a value of 0.507 was computed for steel of one per cent carbon content in the range of temperature covered by this in-

¹ If the curves for the heat of reaction or heat content per gram of mixture are linear with the weight per cent of sulfur, then the corresponding curves per mole of C_5H_8 are linear with the number of atoms of sulfur per gram-mole of C_5H_8 .

vestigation. The steel balls had approximately the same carbon content. The mean heat capacity of the glass used as a core for some of the rubber samples was also determined and was found to be 0.85 joule per gram per °C., which is in practical agreement with the value of 0.84 given in the literature for laboratory Pyrex glass (4).

Since the calorimeter was operated isothermally, its heat capacity was not required for the computation of the results. It was of interest, however, in connection with the precision of the method which is dependent on the amount by which the temperature of the calorimeter is changed by the addition or removal of a given quantity of heat. The heat capacity was of the order of 2300 joules per °C. This means that when a steel ball at 25° C. was dropped into the calorimeter at 175°, the temperature was lowered by about 0.033° C.

HEATS OF REACTION AT 175° AND 25° C. The heats of reaction of different mixtures of rubber and sulfur at 175° and 25° C. are given in Table III. The same results are shown graphically in Figure 3, the heats of reaction in joule per gram-mole of C_5H_8 being plotted against the number of atoms of sulfur per gram-mole of C_5H_8 . This method of expressing the results was adopted because it provides as a basic unit a fixed chemical quantity, C_5H_8 . The convention followed by previous investigators of plotting the heats of reaction per gram of mixture against the composition in percentage of sulfur by weight is equivalent to employing a unit which changes with composition.

The results plotted in Figure 3 may be represented within experimental error by straight lines of different slopes. Discontinuity in the slope occurs for each curve at a composition corresponding to 0.5 atom of sulfur per gram-mole of C_5H_8 . The two portions of the curve representing the heats of reaction at 175° C. are described by the following equations:

$$\Delta H_{175} = -60.0x \text{ kilojoules/gram-mole } C_5H_8$$

for x values from 0 to 0.5 atom of sulfur per gram-mole of C_5H_8 , and

$$\Delta H_{175} = -22.5 - 15.0x$$

for x values from 0.5 to 1.0. Similarly, the two portions of the curve for the heats of reaction at 25° C. are described by the equations,

$$\begin{aligned} \Delta H_{25} &= -55.4x \\ \Delta H_{25} &= -24.8 - 5.8x \text{ kilojoules/gram-mole } C_5H_8 \end{aligned}$$

the values of x lying between 0 and 0.5 for the former equation, and between 0.5 and 1.0 for the latter.

The observations agree with the values given in these equations with a maximum deviation of 2.3, and an average deviation of 0.6 kilojoule per gram-mole of C_5H_8 .

TABLE III. HEATS OF REACTION OF RUBBER-SULFUR MIXTURES

Condition	Composition of Sample			Heat of Reaction ($-\Delta H$), Kilojoules/ Gram-Mole C_5H_8	
	Rubber Per cent	Sulfur Per cent	Atoms/gram- mole C_5H_8 ^a	At 175° C.	At 25° C.
Purified	95.5	4.5	0.100	6.4	5.9
Crude	95.5	4.5	0.100	5.0	4.5
Purified	91.0	9.0	0.210	12.1	11.1
Crude	91.0	9.0	0.210	12.4	11.4
Crude	86.0	14.0	0.346	21.3	19.6
Purified	82.0	18.0	0.467	30.4	28.1
Crude	82.0	18.0	0.467	28.2	25.9
Purified	81.0	19.0	0.499	28.5	26.0
Crude	78.0	22.0	0.599	31.3	27.9
Purified	75.0	25.0	0.708	33.0	28.7
Crude	75.0	25.0	0.708	30.7	26.4
Crude	75.0	25.0	0.708	33.4	29.1
Crude	72.0	28.0	0.826	34.6	29.3
Purified	68.0	32.0	1.00	38.4	31.5
Crude	68.0	32.0	1.00	36.4	29.5
Crude	68.0	32.0	1.00	37.4	30.5

^a The computation of atoms of sulfur per gram-mole C_5H_8 was made as if the rubber were all C_5H_8 .

The heats of reaction may also be expressed in terms of heat units per gram-atom of sulfur. Since the curve which gives the heat of reaction per gram-mole of C_5H_8 as a function of the number of atoms of sulfur per gram-mole of C_5H_8

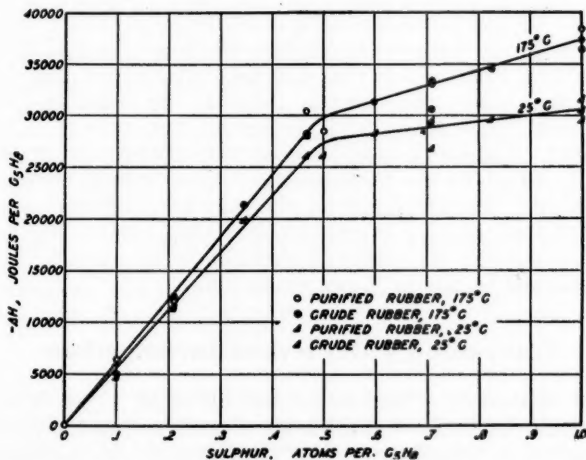


FIGURE 3. RELATION BETWEEN COMPOSITION AND HEATS OF REACTION OF RUBBER-SULFUR MIXTURES AT 25° AND 175° C.

consists of two straight lines corresponding to the two stages of reaction, the heats of reaction per atom of sulfur entering into the respective reactions are constant and are equal to the respective slopes of the two straight lines. The numerical values at 175° C. are -60.0 kilojoules per gram-atom of sulfur for the first-stage reaction which takes place from

$x = 0$ to $x = 0.5$ atom of sulfur per gram-mole of C_6H_8 , and -15.0 for the second stage which takes place from $x = 0.5$ to $x = 1.0$. At $25^\circ C$. the numerical values are $-55.4x$ and $-5.8x$ kilojoules per gram-atom of sulfur for the first- and second-stage reactions, respectively.

In calculating the composition of the samples in atoms of sulfur per gram-mole of C_6H_8 , the rubber, whether crude or purified, was treated as if it were all rubber hydrocarbon. This procedure is warranted, in the present case, by the fact that there is no significant difference in the results for the two kinds of rubber, as shown in Table III and Figure 3. More precise measurements, however, would doubtless indicate a difference, since it is well known that not only the hydrocarbon but also the resins and proteins of crude rubber react with sulfur.

Some experiments were conducted in which rubber-sulfur compounds, vulcanized with less than the maximum amount of sulfur, were further vulcanized with additional sulfur. The quantity of heat liberated was in agreement with the value calculated by subtracting the heat of reaction of rubber with the initial percentage of sulfur from the heat of reaction with the final percentage as read from Figure 3. In one such experiment, vulcanized rubber containing 19 per cent of sulfur ($C_6H_8S_{1/2}$) was ground and mixed with additional sulfur to correspond to a composition of 32 per cent (C_6H_8S). Because of the bulk of the mixture the largest sample that could be used was less than half the ordinary size, and the precision was correspondingly reduced. On vulcanization, the heat liberated was 5.5 kilojoules per gram-mole of C_6H_8 . Figure 3 indicates a value of about 30.0 kilojoules per gram-mole of C_6H_8 for the vulcanization of rubber with 19 per cent of sulfur. The addition of 5.5 kilojoules to this gives a value of 35.5 kilojoules per gram-mole of C_6H_8 , which may be compared with the value 37.5 indicated by the curve for the compound containing 32 per cent of sulfur.

Comparison with Previous Investigations

A comparison of the heats of reaction at $25^\circ C$. which are given in Table III with the heats of reaction found in some previous investigations is shown in Figure 4. In preparing this figure, the convention of previous investigators has been followed in expressing the heats of reaction in joules per gram of mixture and the composition in percentage of sulfur by weight.¹ The results of Kirchhof and Wagner (14) are somewhat higher than those of the present investigation and extend to only 10 per cent of sulfur. These investigators were chiefly concerned with the effect of fillers and accelerators on the heats of vulcanization and reported only a few observations on mixtures of rubber and sulfur alone.

The results of Blake (2) are lower than those of the present

investigation and indicate that the heat of reaction is not a linear function in the range from 0 to 8 per cent of sulfur.

The results reported by Jessup and Cummings (11) agree well with the present results for the range from 0 to 19 per cent of sulfur. Their curve exhibits no discontinuity in the slope at this point; hence their values for the compositions from 19 to 32 per cent of sulfur are higher than the present values. This discrepancy at the higher percentages of sulfur may be due to differences in the conditions of vulcanization employed in the two investigations. The samples used by Jessup and Cummings were vulcanized for about 40 hours at 141° C. in an autoclave containing inert gas under pressure;

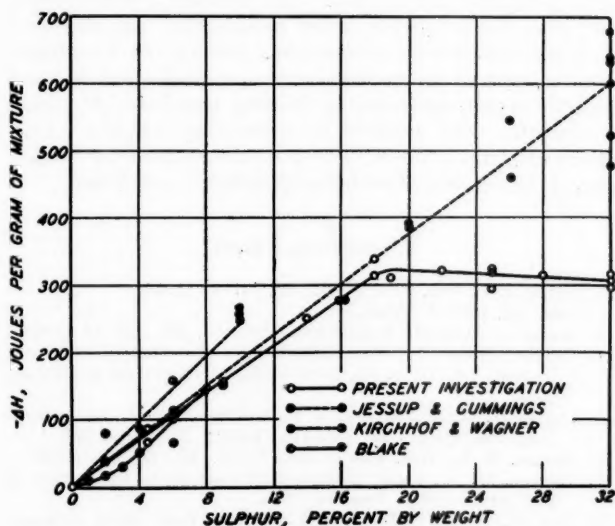


FIGURE 4. RELATION BETWEEN COMPOSITION AND HEATS OF REACTION OF RUBBER-SULFUR MIXTURES DETERMINED BY VARIOUS INVESTIGATORS

in the present work the samples were vulcanized for about one hour at 175° C. in a glass tube, one end of which was open to the air.

The results of an earlier investigation by Blake (1) and of an investigation by Hada, Fukaya, and Nakajima (10) are considerably at variance with those here considered and are not shown in Figure 4 because of the scale used.

A salient feature of this study is the change of slope obtained in the curve for the heat of vulcanization at the composition 0.5 atom of sulfur per gram-mole of C_6H_8 (19 per cent of sulfur by weight). This is an indication that the reaction of rubber with sulfur takes place in two stages, the first liberating a greater quantity of heat than the second. The suggestion of a two-stage reaction between rubber and

sulfur is by no means novel, a variety of evidence for it having been presented by different authors (1, 2, 6, 9, 10, 11, 23). [Curtis, McPherson, and Scott (5) suggested the existence of definite compounds of rubber and sulfur on the basis of changes in electrical properties and density with composition. It was later shown by Kimura and co-workers (12, 13) and by Kitchin (15) that the agreement between changes in electrical properties and the compositions represented by simple empirical formulas was fortuitous and without basic significance.] In some instances the evidence relates to changes in properties which are associated with the fortuitous circumstance that the transition between soft and hard rubber occurs at room temperature at the composition 0.5 atom of sulfur per gram-mole of C_5H_8 . This evidence is shown not to hold when the properties under consideration are measured at other temperatures and pressures. Other types of evidence, however, such as the reaction between vulcanized rubber and alcoholic potash described by Whitby and Jane (22), seem to constitute valid evidence for a two-stage reaction. Definite conclusions, however, cannot be drawn until the mechanism of the reaction of rubber with sulfur is established.

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Dispersion of Channel Gas Black in Rubber

Effect of Stearic Acid and Other So-called Dispersing Agents

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THE completeness of wetting of carbon black by rubber, the consequent state of dispersion of the black, and the effect of the surface forces in the development of reinforcement of the rubber have been the subjects of much deliberation and experimentation. Of special interest has been the effect of stearic acid upon the dispersing power of rubber for carbon black.

On the basis of Green's observation (6) that the dispersion of zinc oxide which had previously flocculated in kerosene resulted in a pronounced softening of the mixture, Goodwin and Park (5) concluded that stearic acid has little effect upon the dispersion of carbon black in rubber. They pointed out that stearic acid has a slight softening action in uncured stock and in cured stock containing no zinc oxide, and that the addition of fatty acid to a stock containing no zinc oxide affects its physical properties adversely. Although they considered that these facts furnished slight indications of a dispersing effect by the stearic acid, these authors offered no convincing evidence of the dispersing effect of stearic acid on carbon black in rubber. For various reasons, including the fact that the plasticity of uncured black stocks is not materially affected by the presence of zinc stearate, Goodwin and Park also concluded that zinc stearate is not a dispersing agent for blacks. In fact, they postulated that the effect of zinc stearate, if any, is to decrease the wetting of the black by the medium and hence to cause flocculation. Since the combined addition of zinc oxide and stearic acid to a rubber-sulfur mix results in an improvement in properties, these investigators were finally led to the conclusion that the principal effect of these soap-forming agents in a carbon black stock is on the curing properties of the rubber itself rather than on the dispersion of the black.

Blake (3) subsequently proposed the interesting hypothesis that there is already present in high-grade plantation sheet sufficient acidic material to form a monomolecular film around each particle of carbon black in a stock containing

30 volume per cent of the pigment. He expressed the belief that the black is wetted by the acidic material and not by the rubber, and that the carboxyl groups of the acids are adsorbed by the carbon particles, while the long hydrocarbon chains are adsorbed or dissolved by the rubber. Although Blake's calculations apparently proved his contention regarding the possible existence of a monomolecular film of adsorbed material around the black, Parkinson (8) has challenged the accuracy of the calculations on the basis of the use by Blake of the value of 200 $m\mu$ for the average size of the carbon black particle. Since this value is undoubtedly too large, the surface area of the black is much greater than that assumed by Blake.

Regardless of the accuracy or inaccuracy of Blake's calculations, the question as to whether or not stearic acid is a dispersing agent for carbon black in rubber is one which can be subjected to experimental study. It would seem that the obvious method of investigation involves the study of the dispersion of black in rubber from which the fatty acids have been removed. The small amount of work reported along this line has yielded contradictory results. Grenquist (7) made the statement that "it was very difficult to disperse the pigments on the mill" when working with acetone-extracted rubber. On the other hand, Parkinson (8) reported that carbon black dispersed just as readily in acetone-extracted rubber as in rubber which had not been extracted.

A few attempts have been made to evaluate possible dispersing agents for black in rubber by observing their effects on carbon black in other media. Thus, Bierer and Davis (2), after repeating and extending the work of Green (6) on the effect of the addition of a dispersing agent to a kerosene-zinc oxide paste, made tests on mixtures of carbon black with kerosene or other vehicles. They found that degas and a certain accelerator [triethyltrimethylenetriamine with stearic acid (50 per cent)] deflocculated the carbon black. Stearic acid, however, was not listed among the agents which had any effect. Depew (4) also studied such pastes and found that both stearic acid and blown poppy-seed oil, which are quite effective in deflocculating zinc oxide, failed to disperse carbon black. Moreover, Parkinson (8) has reported that he failed in various attempts to disperse black in stearic acid itself. The results of tests in other media thus favor the assumption that stearic acid is not a dispersing agent for carbon black.

The work here reported was undertaken with the objects of settling the questions regarding the ease with which carbon black can be dispersed in acetone-extracted rubber and the effect of stearic acid upon the dispersion, and incidentally of discovering if possible whether tests in other media can be used to evaluate the effectiveness of various materials as dispersing agents for carbon black in rubber.

Preparation of Rubber

An extractor of design similar to the Underwriters Laboratory type and of capacity sufficient to hold approximately 25 pounds (11.3 kg.) of rubber was used in this work. For the first tests a large sample of thin pale crepe was selected and divided into two parts. One part was held as a reference control. The other part (approximately 20 pounds or 9.1 kg.) was extracted for 6 days in acetone. The acetone-extractable matter, as determined in a laboratory Soxhlet apparatus with 16-hour extraction, was originally 3.17 per cent. After the 6-day extraction period in the large extractor, this value was reduced to 0.17 per cent. In order to obtain uniform material, the control and the extracted rubber both were milled separately on a clean mill. The other types of rubber, used in the experiments reported later, were treated in the same manner.

Milling of Carbon Black in Extracted Rubber

Samples of carbon black were selected from five different sources, the samples being chosen because of differences in factory operating behavior. Special care was taken to obtain samples of low and nearly identical grit content (as retained on a 325-mesh screen).

The blacks were mixed into both extracted and unextracted rubber, the milling conditions being maintained identical throughout. The composition of the batch used was: rubber 100, carbon black 67. Four hundred grams of rubber were employed in the actual mix.

TABLE I. PLASTICITY AND RECOVERY EFFECTS OF VARIOUS BLACKS IN NORMAL AND EXTRACTED RUBBER

Rubber	Carbon Black	Thickness in Mm. ^a		Increase in Thickness after 3 Days, as Per Cent of Original	Thickness in Mm. after 3 Min. in Press at 120° C.
		After 3 min. in press at 100° C.	After 3-day recovery at room temp.		
Unextracted	A	6.1	7.2	19	5.5
	B	6.3	7.4	19	5.8
	C	5.8	7.2	22	5.5
	D	5.9	7.3	23	5.6
	E	6.8	8.8	27	6.4
Extracted	A	7.6	10.4	37	6.6
	B	7.8	10.4	34	6.8
	C	7.2	10.0	39	6.4
	D	7.4	10.3	37	6.5
	E	7.9	10.8	36	6.8

^a Samples were approximately spherical pellets of 2 cc. volume.

Every effort was made to keep the total time of milling exactly the same in all cases. This time was 13 minutes for all samples except A and B in extracted rubber, and included a uniform period for breakdown of the rubber, a period for addition of black, and a final mixing period. Samples A and B in extracted rubber ran overtime several minutes because of

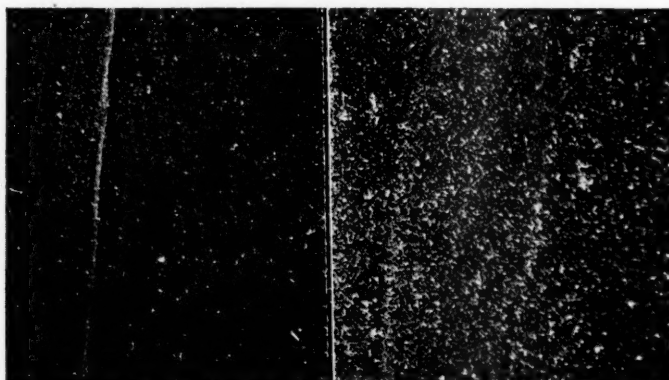
the tendency of extracted rubber mixes to stick to the mill. In spite of this longer milling, which would tend to improve the dispersion, these two batches as well as the other samples were in an exceedingly poor state of dispersion in extracted rubber as compared with their condition in the control rubber.

The actual periods required for incorporation of the black alone are given in the following table:

Sample of Black	Pale Crepe	
	Extracted Min.	Unextracted Min.
A	7	3.5
B	6	4
C	7.5	5
D	6	4.5
E	7.5	4.5

It is evident that the difficulty of incorporation of black was much greater in the case of the extracted rubber.

The appearance of surfaces carefully cut with a sharp knife is exemplified in Figure 1. The difference in smoothness of the two mixes is quite evident. Remilling of the sam-



Carbon black in unextracted rubber Carbon black in extracted rubber
FIGURE 1. APPEARANCE OF SURFACES CUT WITH A KNIFE ($\times 8$)

ples resulted in a proportionally greater improvement in the extracted rubber stock.

Plasticity in Extracted and Unextracted Rubber

Plasticity determinations were made upon the stocks by means of the Williams plastometer. The results are shown in Table I.

It is evident from these data that the mixes containing extracted rubber were definitely less plastic and had more tendency to recover than those mixed with regular rubber.

A second test was run with a new batch of extracted rubber (0.45 per cent extractable residue). The values obtained

for thickness after 3-minute pressing were practically identical with those of Table I. This duplication gave eight separate tests of the comparative effects of the blacks on the plasticity of the stock. The tests agreed quite closely in placing the blacks in the following order of increasing stiffening effect: C, D, A, B, E. This result seemed to be in agreement with factory experience with these blacks.

Examination of Stocks at Higher Magnifications

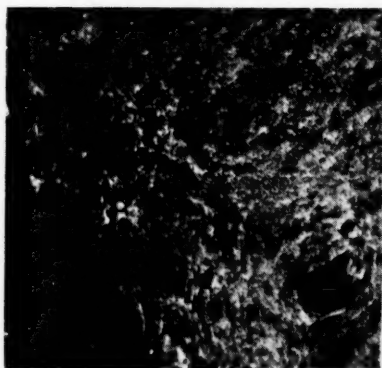
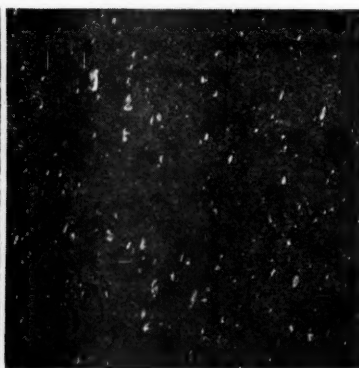
As previously pointed out, the texture of carbon black master batches made with extracted rubber was much rougher than that of the batches containing unextracted rubber. Since this fact was thought worthy of further investigation, mixes of a given black were made in normal rubber, in the same rubber extracted, and in the same extracted rubber to which had been added 4 parts of stearic acid per 100 parts of rubber. Differences similar to those of Figure 1 were obtained, the stock containing stearic acid being equal to the control. Samples of each of these batches were prepared by the method of Roninger (9) and by that of Allen (1). Photographs of these preparations are shown in Figure 2. *A* and *B* show the condition of a batch containing normal rubber. The black spot in *A* is evidently of the same magnitude as the lighter colored discontinuities on the surface of *B*, and both evidently represent zones of higher carbon black concentration. (The black spots in *B* and *D* are pits in the surface.) *C* and *D* show photomicrographs of the same black in the extracted rubber. The light spots on *D* are much more numerous, and the corresponding heterogeneity of *C* is striking. *E* and *F* show sections of the stock made with rubber to which stearic acid had been added prior to incorporation of the black. It is evident that stearic acid had a powerful effect in preventing the inhomogeneity shown. The areas of high concentration of black appear to be somewhat resistant to dispersion by further milling. It has been suggested that these zones are agglomerates of unwet black which have been compacted and mixed into rubber in the form of hard pellets. The writers believe that the individual particles have been wet by rubber, but that because of the concentration of the black the attractive forces between the particles are sufficiently great to resist disruption.

The structure shown bears a close resemblance to the effect produced by so-called scorching of carbon black master batches. Figure 3A shows a photomicrograph of a stock of the following composition:

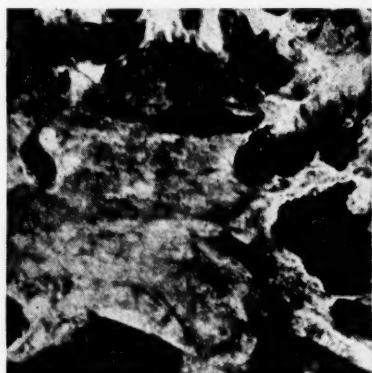
Rubber	100
Super spectra black	84
Stearic acid	14
Phenyl- β -naphthylamine	1.5
Pine tar	5

Allen sections

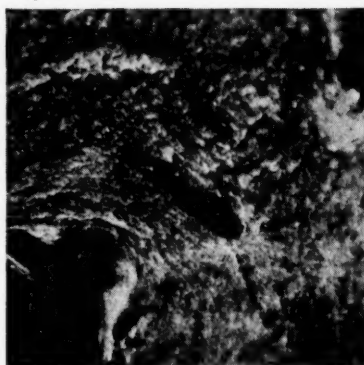
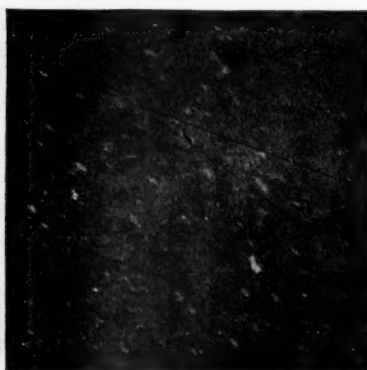
Roninger sections

A ($\times 600$)B ($\times 64$)

Normal rubber

C ($\times 600$)D ($\times 64$)

Extracted rubber

E ($\times 600$)F ($\times 64$)

Extracted rubber plus stearic acid

FIGURE 2. EFFECT OF EXTRACTION OF RUBBER AND ADDITION OF STEARIC ACID UPON CARBON BLACK DISPERSION

This batch, mixed in a factory Banbury mixer, reached the batching-off mill in a scorched condition. Further milling of this material for a 15-minute period produced the result shown in Figure 3B. The original stock consists almost entirely of a network of elongated particles. Although casual inspection of Figure 3B gives the impression that the discontinuities have been largely eliminated, it is believed that the change in appearance is due largely to reduction in size of these discontinuities rather than to their elimination. The figure gives no definite support to this concept, which is suggested as a subject for further investigation. Some basis for this point of view is to be found in the behavior of the batch during remilling, since it continued to be rough and dull in appearance during the whole of the 15-minute period, whereas in the case of a normal batch the additional milling ordinarily produces increased smoothness and glossiness of the stock.

The structure shown in Figure 4A is that of a normal factory-mixed master batch. The same stock after remilling is shown in Figure 4B. The continued milling of this batch appears to have resulted in a more complete elimination of the zones of high concentration. It seems probable from considerations previously presented that the light-colored areas represent black in a more or less complete state of flocculation, and that in scorched rubber-carbon black mixes flocculation has proceeded to the point where deflocculation is extremely difficult.

It was thought possible that the tendency toward poor dispersion in extracted rubber might be made the basis of a test for the dispersing effect of various agents commonly used in the rubber industry.¹

Comparison of Dispersing Agents in Extracted Rubber Medium

As a preliminary to the investigations of this possibility, tests were made to determine whether other grades of rubber could be used just as satisfactorily as the pale crepe previously employed. A sample of smoked sheet, after being extracted with acetone for 7 days in the large extractor, was found to have had its content of acetone-extractable matter reduced from 3.75 to 0.53 per cent. With medium light brown crepe, the acetone-extractable matter was 0.48 per cent after 7 days in the extractor. Extraction was continued for 3 additional days in the case of each of these samples. Milling tests demonstrated that these rubbers behaved similarly to that originally prepared from pale crepe.

¹ It was thought at first that the differences in dispersing properties of the blacks might be emphasized by use of extracted rubber to such an extent that a laboratory procedure might be developed for estimating the dispersing properties of carbon blacks. For some reason this failed to work out, and differences from sample to sample of black were little if any greater than when they were compared in normal rubber.

The quantitative estimates shown in Tables II and III indicate, however, that the various samples of extracted rubber probably did not wet the black to exactly the same degree.

Although in the previous tests 4 parts of stearic acid per 100 parts of rubber had been used, it was thought that the

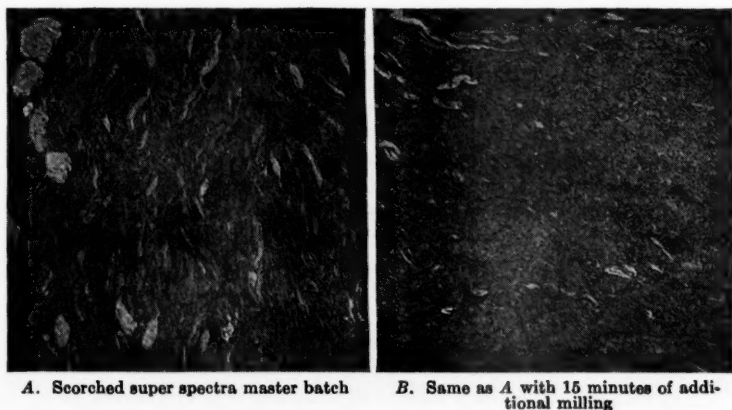


FIGURE 3. EFFECT OF MILLING ON SCORCHED STOCK ($\times 64$)

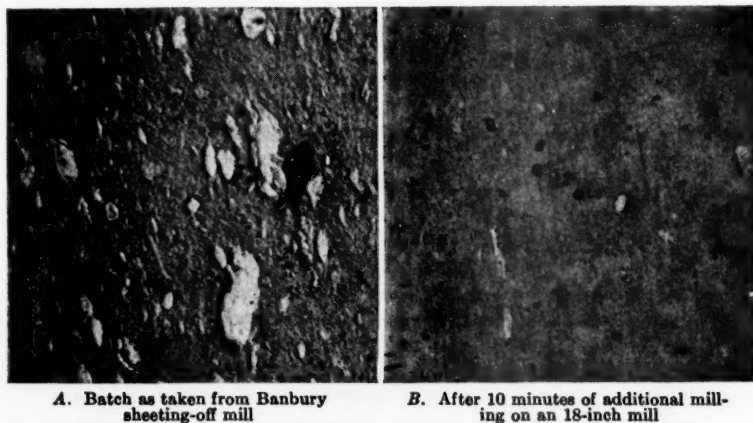


FIGURE 4. EFFECT OF MILLING UPON APPEARANCE OF A NORMAL MASTER BATCH ($\times 64$)

quantity should be reduced in a control stock for use during a comparison of possible dispersing agents. Milling tests with extracted rubber to which but 1 part of stearic acid had been added before the incorporation of the black demonstrated that the resulting stock was smooth (indicating good dispersion) but not quite as smooth as the stock containing 4 parts of stearic acid. On the basis of this result, the basic stock

chosen for use in the comparison of the dispersing agents had the following composition:

Extracted rubber	100
Gas black	67
Dispersing agent	1

The procedure, in the case of the tests made with extracted smoked sheet, was to break down the rubber (a 600-gram batch) for 1.4 minutes on the 12-inch (30.5-cm.) mill before starting the addition of the special agent, begin the addition of the black after a total time of 4.25 minutes, and remove the completed batch after a total time of 13 minutes. The only difference in the case of the tests made with the extracted brown crepe was that a longer time (2.4 minutes) was required for the preliminary breakdown of the rubber. The temperature of the effluent cooling water from the mill rolls was maintained at $126 \pm 1^\circ \text{F.}$ ($52 \pm 0.6^\circ \text{C.}$) during these tests.

As has been previously mentioned, attempts have been made to evaluate possible dispersing agents for carbon black in rubber by means of their deflocculating effect on black in other media. In this laboratory, for instance, a whole series of such tests was made with pastes of gas black in such media as turpentine and dipentene. The latter was used in the hope that its chemical composition would be sufficiently similar to that of rubber so that the results obtained would be more indicative of those to be expected in rubber than are similar tests in a vehicle such as kerosene. The procedure followed was to prepare a relatively large batch of the gas black paste and use small portions of this batch for testing the various agents. Carbon black pastes require larger quantities of dispersing agents for deflocculation than the zinc oxide-kerosene pastes of Green (6) and others. In these tests the dispersing agents were added to the carbon black pastes to the extent of about 10 per cent by volume.

Table II shows the results of dispersion tests made with various possible dispersing agents in acetone-extracted smoked sheet, together with the results of deflocculation tests in turpentine and dipentene made with the same agents. The completeness of dispersion of the black in the various rubber stocks was estimated by macroscopic observations, made independently by each of the writers. The extent of the undispersed areas in the stocks was also estimated quantitatively under the microscope, by the method of Roninger (9).

The results of a similar series of tests made with other agents and with acetone-extracted brown crepe instead of smoked sheet are presented in Table III. The synthetic fatty acid used was a product prepared from petroleum. Lauric-ol is a commercial product containing 45 to 47 per cent lauric acid. Both the accelerator, triethyltrimethylene-triamine, and the commercial product containing this base

with stearic acid (see tests of Bierer and Davis, 2) were used in these studies. The product listed as sulfurized naval stores oil was a sulfurized terpene containing 11 per cent sulfur. Macroscopic estimates of the dispersive effects of the

TABLE II. DISPERSIVE EFFECT OF VARIOUS AGENTS ON GAS BLACK IN ACETONE-EXTRACTED SMOKED SHEET AND OTHER MEDIA

Agent Used	Dispersion in Extracted Rubber				Deflocculating Effect on Gas Black in: Turpentine Dipentene	
	Area of discontinuities, per cent	Microscopic	Order of decreasing dispersive effect ^a			
			Macroscopic			
			In-vesti-gator A	In-vesti-gator B		
			A	B		
None	15.6	5	5	5
Stearic acid	3.6	1	1	1	None	None
Paraffin	17.4	6	6	6
Pine tar	11.1	2	3	3	None	None
Refined asphalt	12.8	4	3	4	Considerable	Considerable
Degras	11.4	2	2	2	Considerable	Considerable

^a The smaller the number, the more complete was the dispersion.

agents listed in Table III were made by seven different observers, all of whom had had considerable experience with gas black compounds.

Of the agents tried with extracted smoked sheet (Table II), only stearic acid showed any appreciable dispersing effect on the black. No difference of consequence between the microscopic and macroscopic estimates of the completeness of dispersion was evident with these agents. In the case of the tests reported in Table III, on the other hand, several of the agents dispersed the black nearly as well as did the stearic acid. Moreover, the discrepancies between the microscopic and the macroscopic observations were much more evident with these agents. In fact, the results indicate that it is impossible by macroscopic observations to distinguish between agents differing only slightly in dispersive effect. In the case of the commercial accelerator, triethyltrimethylenetriamine, accurate observation of dispersion without magnification was rendered difficult by the fact that the accelerator produced roughness in the rubber matrix itself. The reason oleic acid and stearic acid were rated so much lower by macroscopic than by microscopic observation is not apparent.

A comparison of the results of the deflocculation tests in turpentine and dipentene (shown in the last two columns of Tables II and III) with the results of the dispersion tests in extracted rubber demonstrate conclusively that there is practically no correlation between the two phenomena.

As an illustration of the application of the dispersion test in extracted rubber to the evaluation of so-called dispersing agents, the results of tests on four materials recently submitted to this laboratory may be cited. These were com-

TABLE III. DISPERSIVE EFFECT OF VARIOUS AGENTS ON GAS BLACK IN ACETONE-EXTRACTED BROWN CREPE AND OTHER MEDIA

Agent Used	Area of Discontinuities, Per Cent	Order of Decreasing Dispersive Effect in Extracted Rubber ^a					Dedoculating Effect on Gas Black in:	
		as observed by:					Turpentine	Dipentene
		A	B	C	D	E		
None	11.1	7	8	8	6	7
Stearic acid	4.2	1	5	3	7	5	None	None
Synthetic fatty acid	5.4	1	3	5	2	1	...	None
Lauric-ol	5.5	2	2	1	1	6	...	None
Zinc stearate	5.9	1	4	1	2	3	...	None
Oleic acid	7.0	8	7	6	3	8	None	None
Triethyltrimethylenetriamine-stearic acid	7.4	5	1	4	5	1	Considerable	Considerable
Sulfurized naval stores oil	12.3	8	9	9	9	9	...	None
Triethyltrimethylenetriamine	13.8	9	6	7	2	1	None	None

^a The smaller the number, the more complete was the dispersion.

mercial products stated to be (1) cetyl alcohol and stearyl alcohol (1-octadecanol), (2) stearyl glycol, (3) largely oleyl alcohol, and (4) chiefly lauryl alcohol (1-dodecanol) and myristyl alcohol (1-tetradecanol). When they were milled with gas black into acetone-extracted pale crepe in the manner described above, the areas of discontinuities were (1) 9.3 per cent, (2) 6.5, (3) 5.4, and (4) 8.1. The area of undispersed black in a stock containing no added agent was 14 per cent, whereas that in a stock containing stearic acid was practically 0 per cent. Thus, although the special agents showed some dispersive effect, they were all decidedly inferior to stearic acid in this respect. This conclusion was also confirmed by the results of macroscopic observations. Wiegand (10) has reported agents of similar composition to have but little effect on the dispersion of carbon black in rubber.

Discussion of Results

It seems proper in conclusion to elucidate, if possible, the reasons for the discordance with and contradictions to previous work. It seems self-evident that Goodwin and Park (5) were misled regarding the dispersing effect of stearic acid and zinc stearate because the plantation rubber which they used contained ample fatty acid to produce a satisfactory dispersion of the carbon black. Any additional effect of added stearic acid or zinc stearate was probably so small as to escape attention.

It should be pointed out that the findings of this paper do not form the basis for any conclusion regarding the relation between the improved properties produced by stearic acid in vulcanized, accelerated mixes and the improved dispersion of the carbon black. Whatever this relation may be, it is an effect entirely apart from the principal role of stearic acid, which is that of its effect on cure in the presence of zinc oxide.

It is much more difficult to understand the results of Parkinson (8), since he conducted his experiments with extracted rubber. The only explanation which offers itself is that the extraction was not carried sufficiently near completion, and residual fatty acids effected dispersion comparable to that of the control.

Acknowledgment

The writers wish to express their appreciation to N. A. Shepard for permission to publish this paper and also desire to acknowledge the coöperation of F. H. Roninger, Jr., and of P. P. McClellan in connection with the microscopic work.

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Surface Chemistry of Carbon Black

Effect on Vulcanization of Rubber

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CHANNEL carbon blacks retard the rate of cure of rubber compounds. Because the magnitude of this effect varies over wide limits, an elaborate and expensive routine of direct testing of blacks in rubber compounds is necessary to determine their curing behavior. With the hope of eliminating, standardizing, or predetermining the amount of this retardation of cure, numerous technologists, in both the rubber and gas black industries, have investigated the phenomenon. In general, their conclusions are that carbon black retards cure through adsorption. However, interpretations as to what is adsorbed and the mechanism of that adsorption so nearly equal the commentators in number that a critical review of the problem is needed.

History

LeBlanc, Kröger, and Klotz (37) state that it is impossible, from a study of crude lampblack, to predict the properties of rubber-lampblack mixes. They based this statement on their observations that lampblack suspended in an organic medium did not show any adsorptive capacity for sulfur, iodine, or mercaptans. Twiss and Murphy (56) postulate that the retarding effect of gas black on the rate of vulcanization of rubber compounds is the result of adsorption of the natural accelerators present in the rubber. On the other hand, Ditmar and Preusse (18) state that this retardation of cure is due solely to the removal of sulfur by the black. Dinsmore and Vogt (17) state that the carbon black exerts its greatest effect on the accelerator, but that in mercaptobenzothiazole stocks the carbon black retards cure apparently by adsorbing the resin acids. Spear and Moore (54, 55) found some evidence that the differences in the adsorption of hexamethylenetetramine from benzene by various carbon blacks paralleled the differences in time of cure of rubber compounds containing these blacks.

Goodwin and Park (26, 27) showed that high-color blacks, rubber blacks, and certain thermal-decomposition blacks gave different adsorption isotherms with iodine and methylene

blue solutions in water and in carbon tetrachloride. They believe that a highly adsorptive black removed curing agents from the rubber. In the presence of carbon of the channel black type, larger amounts of stearic acid must be added because the black behaves as if it removed stearic acid from the field of action, although the effect is probably more complex. Carson and Sebrell (14) attempted to correlate the curing properties of a black and its iodine adsorption. They present as an anomaly a heated black with an increased iodine adsorption but a decreased retarding action on cure. Fromandi (22) determined the adsorption isotherms of various blacks for acetic acid but presented no correlation with curing properties. Beaver and Keller (8) showed definitely that blacks retard the rate of cure of rubber stocks in direct proportion to the amount of oxygen held on their surface. Johnson (28) found that, when the volatile matter of a rubber black is above a certain limit for that variety, its reinforcing effect in rubber compounds is smaller and the rate of cure of the stock is slower. Later Johnson (29) correlated this retardation of cure with the oxygen content of the black, stating that high volatile matter or oxygen content is indicative that such carbon black will yield stocks of poor physical properties because it will adsorb more organic accelerator than the normal black.

The work of Drogin (19) and of Wiegand (57) led to the development of the alcohol-diphenylguanidine adsorption test for carbon blacks, which in some cases assisted the producers to predetermine the effect of the blacks in rubber. Amon and Estelow (3) used a solution of diphenylguanidine in benzene, claiming a manipulative advantage for benzene over alcohol. Wiegand and Snyder (58) applied the alcohol-diphenylguanidine adsorption test to a large number of special blacks and concluded that the test indicated qualitatively, but does not predict with precision, the rubber-compounding behavior of the commercial blacks.

Adsorption

If the retardation of the cure of rubber compounds containing gas black is a function of the adsorptive characteristics of the black, this adsorption must be of one or more of the following types:

1. Pure physical adsorption, in which the adsorbed material is completely recoverable by lowering its concentration in the surrounding medium or by raising the temperature of the system.
2. Activated adsorption, in which, probably because of the formation of a molecular complex with the adsorbent, the adsorbed material is at most only partially recoverable.
3. Solution, in which the adsorbed material dissolves in the adsorbent.

PHYSICAL ADSORPTION. Physical adsorption takes place at low temperatures and is usually ascribed to van der

Waals' forces. Such forces tend to decrease exponentially with increase of temperature. That carbon black does not remove, at ordinary milling and vulcanizing temperatures, an appreciable quantity of curing agents by this type of binding is clearly shown by the behavior of the heat-treated blacks that Carson and Sebrell (14) present as anomalous to the adsorption theory. These blacks were prepared by heating

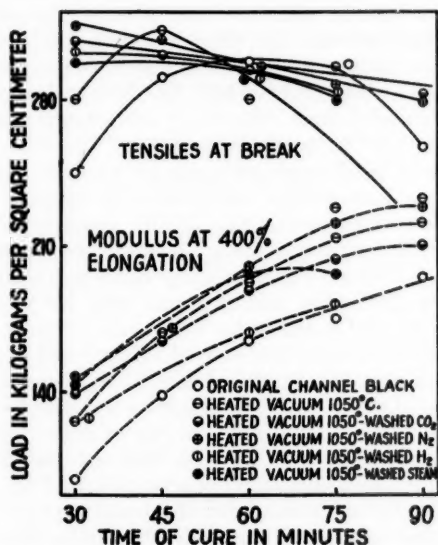


FIGURE 1. CURING BEHAVIOR OF TREATED CHANNEL BLACKS ON A D. P. G.-ACCELERATED STOCK

carbon black in large covered crucibles in an electric furnace at 900° to 1000° C. for 10 to 60 minutes. Such treatment should activate the blacks—i. e., increase their physical adsorptive capacity. That the heat treatment actually did this was evidenced by an increase in the iodine adsorption. However, when these highly adsorptive blacks were compounded into rubber, a faster rate of cure was obtained than with the untreated carbon black.

Determination of Effect of Physical Adsorption. A channel black was treated so as to vary its adsorptive capacity. The methods of treatment and the capacity of the resulting treated blacks for adsorbing iodine are detailed in Table I. The iodine adsorptions were determined by the method of Carson and Sebrell (14); the standard iodine solution was 0.0898 N and the standard thiosulfate solution was 0.0988 N. Heating the black in a vacuum permits distillation of the impurities; this leaves a cleaner surface as is evidenced by increased iodine adsorption. Washing heated black with a stream of car-

bon dioxide or with steam increases the physical adsorptive capacity of the black, inasmuch as these materials scour the surface free of impurities and react with the carbon to yield gases which distill off, leaving a fresh and probably a larger surface. Washing heated black with nitrogen or hydrogen also cleans the surface free of impurities. However, the iodine adsorption capacity of the nitrogen- and the hydrogen-washed blacks is less than that of the untreated sample. The reason for this behavior is not obvious, but free energy considerations indicate that there is no reaction between carbon and nitrogen at any temperature and no reaction between carbon and hydrogen above 500° C. The hydrogen-treated black was cooled from 500° C. to room temperature sufficiently rapidly to preclude reaction. Therefore, in the treatment of black with hydrogen or nitrogen there is no tendency to increase the surface area by chemical reaction as there is with carbon dioxide or with steam. On the contrary there is a tendency toward a smaller surface area inasmuch as the black may sinter slightly at the high temperatures used. Also hydrogen and nitrogen may be adsorbed in amounts sufficient to reduce the iodine adsorption.

If the retardation of the cure of rubber stocks by carbon blacks is an example of physical adsorption, then the relative adsorption of iodine by blacks would be a measure of this retardation. This follows from the rule of equivalents as expressed by Freundlich (20). Also Michaelis and Rona (43) obtained for adsorbents differing as widely as blood charcoal, talc, and sulfur the same order of adsorption for a series of alcohols and acetone. Freundlich (21) quotes from unpublished work of H. Fisher who found that a series of charcoal preparations, partly of technical and partly of laboratory origin, always fell in the same order in their ability to adsorb a wide variety of materials. As long as physical adsorption only is involved, the rule of equivalency appears to hold. On the basis of physical adsorption, a stock containing black activated by heating in a vacuum, carbon dioxide, or steam, would be slower curing than one with untreated black; and stocks containing black treated with nitrogen or hydrogen would be faster. The results obtained by compounding these blacks in the following diphenylguanidine-accelerated test recipe are shown in Figure 1:

Smoked sheets No. 1	100.0	Stearic acid	2.1
Carbon black	40.0	Diphenylguanidine (D. P. G.)	0.75
Zinc oxide	6.0		
Sulfur	5.4		154.25

All the heat-treated blacks show an increased rate of cure regardless of their physical adsorptive capacity. Therefore, physical adsorption is not the dominating factor in the retardation of cure by carbon black.

The astonishing degree to which slow-curing blacks can be improved by heat treatment is shown in Figure 2. The

material is an ink black in the diphenylguanidine recipe just mentioned. In general, after treatment the black imparts to the stock higher moduli at 400 per cent elongation than the tensiles at break of the stock containing untreated black.

ACTIVATED ADSORPTION. Activated adsorption takes place at high temperatures. The velocity of this type of adsorption process increases to an equilibrium maximum with an increase in temperature. At temperatures higher than the equilibrium temperature the molecular complex decomposes faster than it is formed. This behavior points toward the presence of an activation energy which provides an explanation for the absence of this type of adsorption at low tempera-

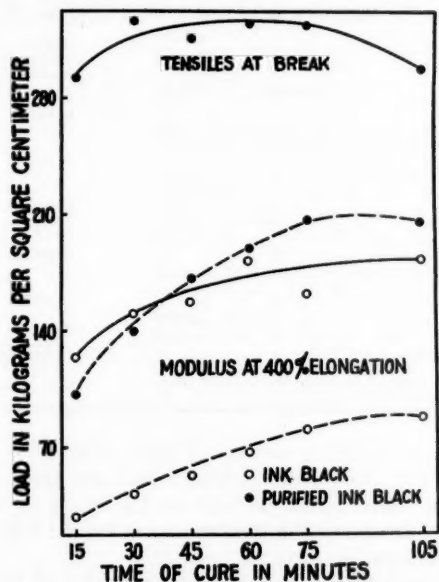


FIGURE 2. EFFECT OF HEAT TREATMENT ON A SLOW-CURING BLACK

tures. A mechanism of this type might cause the retardation of cure by carbon black. For example, carbon black probably forms on its surface a molecular complex when heated with sulfur. If sulfur and black are heated together, hydrogen sulfide comes off. This is produced by reaction between sulfur and hydrocarbons in or on the black according to the reaction:



It can be shown thermodynamically that this reaction can go to completion above the melting point of sulfur. Nellensteyn and Thoenes (47) report that the reaction between sulfur and paraffins, paraffin oils, or lubricating oils at 260° to

300° C. yields carbon and almost all sulfur as hydrogen sulfide, with only traces of organic sulfur compounds. They report that sulfur will completely break down $-\text{CH}_2=\text{CH}_2$, and $\equiv\text{CH}$ groups. By heating commercial carbon blacks with sulfur, the hydrocarbon hydrogen is converted to hydrogen sulfide which is easily estimated.

Determination of Effects of Activated Adsorption. A sulfur-bearing black was produced by heating an intimate mixture of equal weights of channel black and sulfur for 2 hours at 300° C. The free sulfur was extracted with acetone in a Soxhlet type apparatus. After several days of extraction of

TABLE I. SURFACE TREATMENT OF A CHANNEL BLACK

Sample	Treatment	Iodine Adsorption, Grams per Gram Black	Relative Adsorption
1	None	0.04912	100
2	Heated in vacuum ^a to 1050° C., held in vacuum at 1050° C. for 24 hours; cooled in vacuum	0.09752	198
3	Heated in vacuum to 1050° C., washed with CO_2 at 1050° C. for 24 hours; cooled in stream of CO_2	0.08152	168
4	Heated in vacuum to 1050° C., washed with N_2 at 1050° C. for 24 hours; cooled in stream of N_2	0.03256	66
5	Heated in vacuum to 1050° C., washed with H_2 at 1050° C. for 24 hours; cooled in stream of H_2	0.03856	79
6	Heated in vacuum to 1050° C., washed with steam at 1050° C. for 24 hours; cooled in vacuum	0.10112	209

^a In all cases the vacuum was less than 1 mm. Hg.

the black, a negligible amount of sulfur was being removed although the black still contained 2.61 per cent of sulfur. This sulfur must either be held on the black by activated adsorptive forces, or the treatment has caused the sulfur to assume an insoluble form.

In Figure 3 is shown the curing behavior of this sulfur-bearing black in the following polybutyraldehyde-aniline (Pullman) tread recipe:

	Balanced Recipe	Adjusted Recipe	Unbalanced Recipe
Smoked sheets	100.00	100.00	100.00
Polybutyraldehyde-aniline	1.20	1.20	1.20
Sulfur	2.00	0.75	0.75
Zinc oxide	5.00	5.00	5.00
Lauric acid	2.00	2.00	2.00
AgeRite powder (phenyl- β -naphthylamine)	0.75	0.75	0.75
Carbon black	47.50	...	47.50
Sulfur-bearing black	48.75
	158.45	158.45	157.20

The upper curve is for the balanced compound containing untreated black and 2 per cent powdered sulfur on the rubber. The adjusted compound contains the sulfur-bearing black and a proportionally decreased amount of powdered sulfur,

the total sulfur being the same as in the balanced recipe. The unbalanced recipe contains untreated black and the same amount of powdered sulfur as the adjusted recipe. These physical data show that the sulfur on the black is apparently inert since the stock containing the sulfur-bearing black duplicates in ultimate tensile at break the stock containing untreated black and the same amount of powdered sulfur. However, while black may activatedly adsorb sulfur, and while such sulfur is inert in a rubber stock, this phenomenon is not the dominant factor in the retardation of cure by carbon black. The compound containing the sulfur-bearing black has the fastest rate of cure. Heating the black with sulfur has altered the black's surface characteristics so that its behavior in rubber resembles that of the heat-treated blacks previously discussed.

SOLUTION. Solution is the result of diffusion into the interior of the solid. This process is slow and, according to the work of Lenard-Jones (38), requires an activation energy. For this reason it resembles and may be confused at high

temperatures with activated adsorption. It does not seem possible, at vulcanizing and milling temperatures, sufficient sulfur or curing agents could diffuse into carbon black to affect materially the rate of cure of rubber stocks. It must, therefore, be concluded that, if adsorption is involved in the effect of gas black on rubber compounds, it is adsorption of the activated type. The compounding tests with heat-treated blacks indicate that such treatment either alters the adsorptive characteristics of black or removes cure-retarding impurities from black. As will be shown, the evidence favors the latter interpretation.

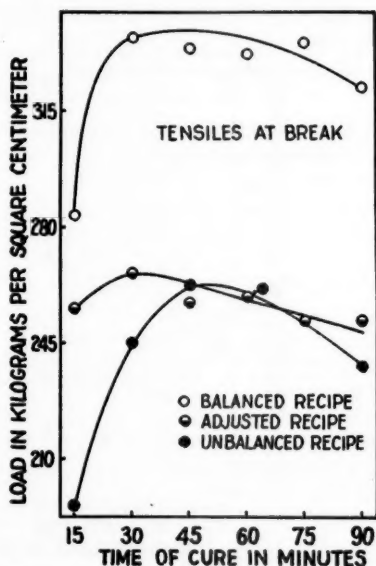


FIGURE 3. CURING BEHAVIOR OF SULFUR-BEARING BLACK ON PULLMAN TREAD STOCK

Impurities on Gas Black

Rubber gas blacks are not pure carbon. The pyrogenic

decomposition of aliphatic hydrocarbons of low molecular weight to form gas carbon produces a material which contains, in addition to the carbon, various organic bodies and adsorbed gases.

REMOVAL OF NONACIDIC ORGANIC COMPOUNDS. By heating the black in a vacuum or by benzene extraction, a reddish to gray-green tar, amounting in most cases to only a fraction of one per cent, is removed. From this tar many crystalline organic compounds varying in color from a deep red to a light yellow can be isolated. They are neutral bodies insoluble in water and most soluble in aromatic hydrocarbons. These materials have been incorporated into rubber in amounts up to 0.5 per cent with no effect on the rate of cure.

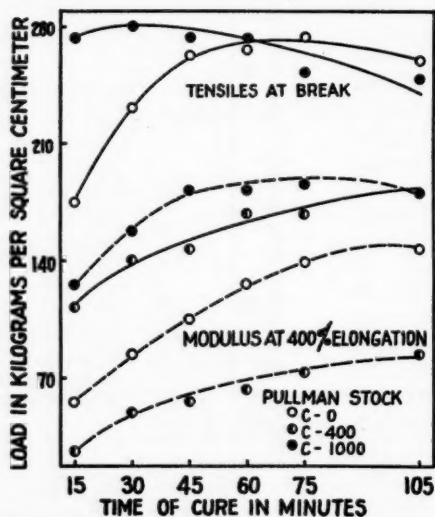


FIGURE 4. RESULTS OF CURE WITH TREATED BLACKS IN A PULLMAN STOCK

The black from which the hydrocarbons were removed by benzene extraction showed no change in curing characteristics. When, on the other hand, the hydrocarbons were distilled off at elevated temperatures under a vacuum, carbon dioxide and carbon monoxide were also evolved. The resulting black produced stocks of higher tensile strength, stiffer modulus, and faster rate of cure. Consequently, the existence on the black of some impurity which is not extractable by benzene, which contains oxygen and which affects the rate of cure of rubber was suspected.

OXYGEN. As early as 1814, DeSaussure (15), one of the first investigators to make quantitative measurements of adsorption by charcoal, recognized the anomalous behavior of oxygen in the presence of carbon. In his adsorption experiments he failed to obtain results for oxygen similar to those for

other gases, since apparently no equilibrium was reached even after one year. Two other early workers verified this observation. Kayser (30) found that the adsorption of oxygen did not cease after two weeks and Böhm (9) found that, while nitrogen adsorbed on charcoal could be completely removed, oxygen could be removed only partially. Allmand and Chaplin (1) state that the adsorption potential of carbon surfaces appears to vary from point to point with the high potential centers initially poisoned by residual oxygen. According to Allmand and Puttick (2) this oxygen can be removed by flushing with carbon tetrachloride vapor and evacuating. So tightly is this residual oxygen held to the carbon surface and so greatly does it affect the adsorption of other materials that there has lately arisen doubt as to the validity of the results of most adsorption studies on charcoal carbons. This has been discussed by Burrage (10, 11).

Probably the first worker to notice that oxygen adsorbed on a carbon surface underwent a chemical change is Smith (53) who in 1863 found that the adsorption of oxygen continued for at least a month and that, when it was sought to remove the oxygen by heat, carbon dioxide was given off instead of oxygen. In 1867 Baker (4) verified this observation. Dewar (16), however, showed that oxygen can be physically adsorbed on carbon at low temperatures. Rhead and Wheeler (48, 49) found that at temperatures up to 900° C. and probably above, carbon retains oxygen so firmly that it cannot be removed by evacuation alone, both an increase in temperature and evacuation being required. When quickly released, the oxygen is not removed as such but as carbon monoxide and carbon dioxide, their proportions depending on the temperature at which the oxygen was "fixed." No physical explanation alone can account for this fixation. Consequently, Rhead and Wheeler assumed that the first product of combustion of carbon is a "loosely formed physico-chemical complex which may be regarded as an unstable compound of carbon with oxygen," whose composition varies. At a given temperature the complex decomposes into carbon dioxide and carbon monoxide in a definite ratio. Evidently oxygen can combine with carbon in several ways; for Langmuir (36) found that a complex of carbon and oxygen, presumably an extremely stable oxide, was formed by a highly graphitized filament of very pure carbon. This particular oxide decomposed slowly at 1425° C. but readily at 1925°, and seemed to be even more stable than the complex formed between oxygen and amorphous carbon. Lowry and Hulett (39) studied the anomalous behavior of the adsorption of oxygen by charcoal and showed it to be caused by the presence of two effects, adsorption and surface combination. Further, they showed that a carbon-oxygen complex, essentially a stable oxide of carbon, could be formed on the surface of charcoal at ordinary temperatures. This complex decomposes to carbon dioxide

and carbon monoxide on heating. Náray-Szabó (46) assumed that the potential of carbon-oxygen electrode depends upon the formation on the surface of a solid oxide (he considers it to be C_3O) which is decomposed by water with formation of ions. Rideal and Wright (50) postulate from the behavior of charcoal and oxygen at different temperatures that there are at least three surface oxides: one removable at high temperatures as carbon monoxide and carbon dioxide, a second removable on evacuation as carbon dioxide, and a third removable at low temperatures as oxygen.

Lamb and Elder (35) obtained a test for peroxide on char-

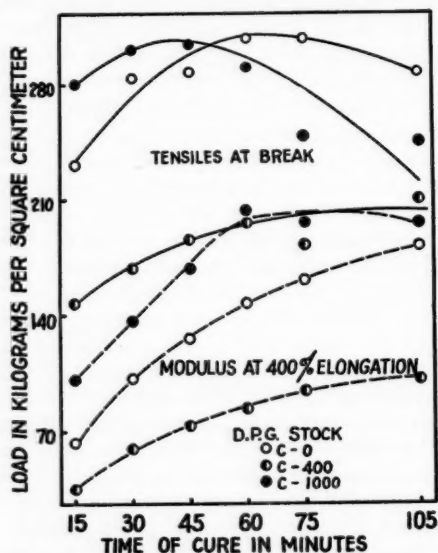


FIGURE 5. RESULTS OF CURE WITH TREATED BLACKS IN A D. P. G. STOCK

coal. Shilov (51, 52) and his co-workers, from the form and position of the isotherm representing the adsorption of hydrogen chloride, deduce the existence of two basic oxides on the surface of carbon; further, they find an acidic oxide when the charcoal is heated to 400-700° C. King (31) extracted ash-free sugar charcoal with boiling water and obtained oxalic acid. This evidence for the probable existence on carbon blacks of an oxygen compound or compounds and the observation of Beaver and Keller (8) and also Johnson (28, 29) that the retarding effects that gas blacks have in rubber compounds are a function of the oxygen content of blacks, give an important clue to the mechanism of the retardation phenomenon. Further, the results obtained by Carson and Sebrell (14) with heat-treated black, as well as unpublished work by R. P. Allen and also by B. S. Taylor and L. M. Freeman on improving slow blacks by heating, give added support

to the belief that it is a carbon-oxygen complex that is responsible for the retarding behavior of blacks in rubber compounds.

There is evidence for the belief that the carbon-oxygen compound influences the adsorptive behavior of carbons. Bartell and Miller (5, 6, 7, 44, 45) have presented data in support of a theory of hydrolytic adsorption of electrolytes from solution by activated ash-free charcoal. Wiegand and Snyder (58, 59) state that heat-treating commercial blacks in the absence of oxygen reduces the blacks adsorptive activity

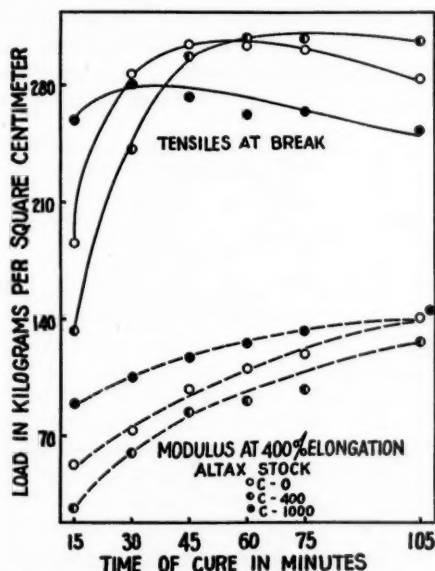


FIGURE 6. RESULTS OF CURE WITH TREATED BLACKS IN AN ALTAX STOCK

toward diphenylguanidine and increases its activity toward hydrochloric acid. Of the many investigations on hydrolytic adsorption, that of Kruyt (33, 34) has a direct application to the present problem. Kruyt finds that low-temperature activation of sugar charcoal is equivalent to slow combustion in which carboxyl groups are formed and give to the charcoal a negative charge and the ability to adsorb hydroxyl ion. At 800° to 900° C. these carboxyl groups are no longer stable. The surface, freed from these groups, adsorbs hydrogen ions and acquires a positive charge in pure water. Heating with oxygen at lower temperatures causes reformation of carboxyl surface groups and reverses the charges. Charcoal heated at 1000° C. in a high vacuum loses its surface-bound oxygen. Admission of oxygen after cooling results in the formation of carboxyl groups and the charcoal then has a positive charge.

Frumkin (12, 13, 23, 24, 25) and his students claim that out-gassed charcoal will not adsorb either ion from solution, but that after outgassed charcoal is allowed to come in contact with oxygen, it acts as an oxygen electrode and adsorbs acids. Kolthoff (32) was able to prepare a positive black by heating at 950° C. and a negative black by heating in oxygen at 400° C., thus checking the work of Krut.

Effect of Carbon-Oxygen Complex on Cure. A commercial black, used as a control, is labeled "C-O." This black cleaned by heating in nitrogen to 1000° C. and cooling in nitrogen to room temperature is designated "C-1000." Another sample heated in a stream of air at 400° C. is identified as "C-400." Portions of these three types of black were passed through a 200-mesh screen. One-gram samples of each were shaken for 2 hours with 100 cc. of 0.01 N sodium hy-

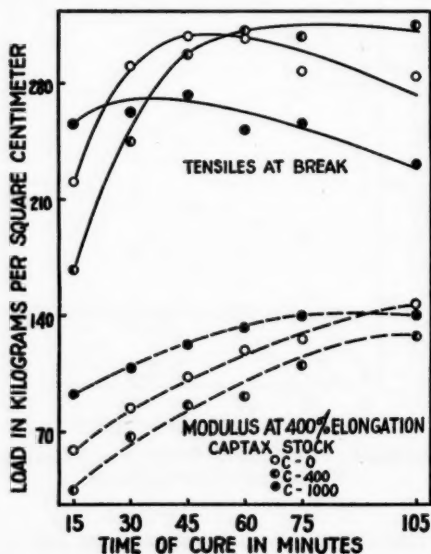


FIGURE 7. RESULTS OF CURE WITH TREATED BLACKS IN A CAPTAX STOCK

dioxide, and similar samples were treated in same fashion with 0.01 N hydrochloric acid. The mixtures were centrifuged and aliquot portions of the supernatant solutions were titrated with standard acid or alkali. The milliequivalents adsorbed by one gram of black are as follows:

Sample	HCl	NaOH
C-O	0.022	0.224
C-400	0.015	0.418
C-1000	0.036	0.092

Treating black so as to increase its oxygen content decreases the amount of acid and increases the amount of alkali that it

will remove from solution. Conversely, removing oxygen from the black increases the amount of acid and decreases the amount of alkali that it will remove from solution. Therefore, oxygen apparently is activatedly adsorbed by carbon to form a molecular complex that is removable at high temperatures and is acidic in character.

These blacks offer the opportunity of determining whether the retardation of cure by carbon black is an example of a hydrolytic type of adsorption. Figures 4 to 7 show the results of cures with the following polybutyraldehyde-aniline (Pullman), diphenylguanidine (D. P. G.) and dibenzothiazole-disulfide (Altax), and mercaptobenzothiazole (Captax) test recipes with these blacks:

	Pullman	D. P. G.	Captax	Altax
Smoked sheets	100.00	100.00	100.00	100.00
Stearic acid	3.20	2.10	3.20	3.20
AgeRite powder	0.75	0.75	0.75	0.75
Zinc oxide	5.00	6.00	7.80	7.80
Pine tar	1.60	1.60	3.20	3.20
Accelerator	0.50	0.75	0.75	0.75
Sulfur	3.25	5.40	3.20	3.20
Carbon black	40.00	40.00	40.00	40.00
	154.30	156.60	158.90	158.90

In the alkaline-accelerated stocks (Pullman and D. P. G.) the black freed from oxygen gives fast cures, high moduli, and tensile strengths comparable to those produced by the untreated black. The oxygenated black gives slow cures, low moduli, and low tensile strengths. These results could be explained on the basis of the selective adsorption theory. However, in the acid-accelerated stocks (Altax and Captax) the black freed from oxygen also gives fast cures and high moduli but low tensile strengths. If adsorption were the dominant factor in cure retardation, the stearic acid removed by the oxygen-freed, high-acid-adsorbing black would cause a retardation in the rate of cure of these stocks. The oxygenated low-acid-adsorbing black gives slow cures and low moduli but high tensile strengths that exceed even those of stocks containing untreated black. These results are not explainable on the basis of the selective adsorption theory. To recapitulate, the black that removes the largest amount of alkali and the smallest amount of acid from solution retards both acid- and alkali-accelerated stocks; the black that removes the smallest amount of alkali and the largest amount of acid accelerates the cure of both acid- and alkali-accelerated stocks; the black containing the greatest quantity of acid complex, C-400, definitely reduces ultimate physical properties of acid-accelerated stocks. Organic acid retarders of cure, such as benzoic acid, have a similar action in rubber compounds. This leads to the supposition that carbon black contains organic acid impurities or has adsorbed on its surface carboxyl groups that cause the black particle itself to act like an organic acid.

If this analogy between the retardation of cure by channel black and by organic acids is correct, it is necessary that all the heat-treated blacks, described under the discussion of physical adsorption, have a lower alkali and a higher acid adsorption than the untreated black, regardless of the fact that the iodine adsorption of some of these blacks is higher and of others lower than the untreated sample. That this is true is shown in the following table:

Sample No.	Iodine Adsorption, Gram per Gram of Black	Milliequivalents Adsorbed by 1 Gram of Black	
		Alkali	Acid
6	0.10112	0.102	0.100
2	0.09752	0.134	0.062
1 ^a	0.04912	0.224	0.022
5	0.03856	0.102	0.034
4	0.03256	0.092	0.036

^a Untreated black.

The preceding discussion has brought out the following points:

1. Oxygen combines with black to form a molecular complex removable only at high temperatures.
2. This carbon-oxygen complex influences the curing behavior of the black.
3. The carbon-oxygen complex influences the curing behavior of rubber stocks in the same manner as an organic acid retarder of cure.

ISOLATION OF THE ACIDS. It is reasonable to expect that, when carbon black is formed by the incomplete combustion of petroleum gases, a small but appreciable portion of them will, under the influence of heat and the catalytic effects of finely divided carbon, be oxidized to organic acids. That channel black can act catalytically in such oxidations is easily demonstrated by moistening black with alcohol and drying it with free access to air at about 100° C. Almost immediately a very irritating aldehyde odor is observed. This odor becomes stronger as the temperature is raised and the surface exposed to air is increased.

Another source of acids is the oxidation of carbon itself which produces the anhydrides of mellitic acid. Mellitic acid was made from various commercial blacks by oxidation with nitric acid of 1.5 specific gravity. In general, the technic of Meyer and his co-workers (40, 41, 42) was followed. Considerable heat is evolved during this oxidation, and the speed of the reaction is inversely proportional to the particle size of the black. With a channel black, great care must be exercised to prevent spontaneous combustion in the nitrogen oxides at temperatures even as low as 40° C. Mellitic acid, in common with other carboxylated benzene compounds, has been proved by test to retard the rate of cure of rubber stocks. Probably because of low solubility in rubber, its effect is much less than with benzoic or phthalic acids.

From the results of work in the vapor-phase oxidation of

petroleum, it would not be surprising if commercial channel blacks contained a number of aliphatic and aromatic mono-, poly-, hydroxy-, and aldehyde acids.

Removal of Acidic Organic Compounds. If there are acids on black it should be possible to extract them by treating the black with alkaline solutions. The most successful extraction was made by stirring a mixture of black and concentrated ammonium hydroxide at room temperature for several hours and then filtering off the black. The filtrate was evaporated to dryness under reduced pressure at temperatures below 50° C. The residue was dissolved in 95 per cent alcohol and filtered free from dirt. The solution is golden yellow in color and is neutral. If a vacuum is formed over this solution ammonia gas escapes and it becomes acid. Concentration causes the crystallization of a number of organic acids. In color reactions and general chemical behavior, one of these acids is similar to mellitic acid made by oxidizing channel black with concentrated nitric acid. Other organic acids are present also. Either these organic acids must exist on the black as such, or carbon black can be oxidized to organic acids by treatment with dilute alkali (in some experiments 0.01 *N* sodium hydroxide was used) at room temperatures. The positive identification of these acids and the mechanism of their behavior in rubber will be presented in the next paper of this series.

Conclusion

In an attempt to develop a theory for the retardation of the rate of cure of rubber stocks by carbon black the adsorption theory is critically reviewed. Experimental evidence is presented that is not readily explainable on the basis of this theory. It is shown that the retarding action of gas black is analogous to the action of organic acid retarders of cure. The mechanism of this action is unknown. Gas black activatedly adsorbs oxygen to form an acid complex that retards the cure of rubber compounds. Organic acids have been obtained from commercial blacks by washing with alkalies.

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CORRECTION

The Effect of Surface-Active Substances and Electrolytes upon the Crystallization of Sulfur from Rubber Solutions

B. Dogadkin and J. Margolina

In an article with the above title in RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 8, No. 2, pages 250-8, April, 1935, two paragraphs at the top of page 251 should read as follows:

It is evident that the greater the rate of increase in the formation of nucleus W (based on the number of nuclei which are formed in a given time), the finer and more uniform will be the precipitate under otherwise equal conditions. On the other hand, the increase in the rate of growth V of the individual crystals leads to the formation of a coarse crystalline precipitate. In this way it is theoretically possible to control the crystallization process and to obtain crystals of any desired size.

However, in practice such a control of simultaneous and interdependent processes is very difficult; for a comparison of the two equations shows that an increase in the degree of saturation of the system accelerates both processes. As the results of numerous experiments by von Weimarn have shown, the first process predominates over the second only for high states of saturation ($Q - L$), and also for low values of the solubility L , whereby a finely crystallized precipitate is obtained, *e. g.*, the formation of gels of calcium phosphate, which are obtained by mutual decomposition of concentrated solutions of calcium chloride and sodium phosphate. If, however, the saturation value ($Q - L$) and ($C - l$) is low, and granted that there are no significant changes in one direction or the other, there are very narrow limits to the influence of a change in the saturation of the system upon the crystallization process.